ผลของเชื้อเพลิงผสมไบโอดีเซลต่อสารมลพิษไอเสียของเครื่องยนต์ดีเซล

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EFFECTS OF BIODIESEL BLENDED FUELS ON EXHAUST EMISSIONS OF DIESEL ENGINE

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งานวิจัยนี้ทำการศึกษาผลของเชื้อเพลิงผสมไบโอดีเซลต่อสารมลพิษไอเสียของเครื่องยนต์ดีเซล เชื้อเพลิงทดสอบคือ เมทิสเอสเทอร์ของปาล์มสเตียรินและน้ำมันเมล็ดแรพ   ส่วนผสมของเมทิสเอสเทอร์ของปาล์มสเตียรินและน้ำมันเมล็ดแรพ ในอัตราส่วนร้อยละ 2 5 20 และส่วนผสมของเมทิลเอสเทอร์ของน้ำมันพืชที่ผ่านการประกอบอาหารแล้วในอัตราส่วนร้อยละ 20 30 และ 40 รถยนต์ทดสอบคือโตโยต้าและอีซูซุ   การทดสอบสารมลพิษไอเสียจะทดสอบโดยไดนาโมมิเตอร์ พบว่าสารมลพิษไอเสียและอัตราการสิ้นเปลืองน้ำมันของเมทิสเอสเทอร์ของปาล์มสเตียรินและน้ำมันเมล็ดแรพในอัตราส่วนร้อยละ 2 และ 5 ไม่มีความแตกต่างกับน้ำมันดีเซลอย่างมีนัยสำคัญ แต่ส่วนอัตราส่วนผสมร้อยละ 5 มีแนวโน้มที่จะทำให้สารไฮโดรคาร์บอนและสารมลพิษอนุภาคในไอเสียมีปริมาณลดลง ส่วนผสมของเมทิลเอสเทอร์ของน้ำมันทั้ง 3 ชนิดในอัตราส่วนร้อยละ 20 ทำให้สารไฮโดรคาร์บอน และ สารมลพิษอนุภาคในมลพิษไอเสียลดลง 10 – 34% และ 6 – 34% ตามลำดับ ส่วนผสมเมทิลเอสเทอร์ของน้ำมันพืชที่ผ่านการประกอบอาหารในอัตราส่วนร้อยละ 30 40 ทำให้สารไฮโดรคาร์บอนและสารมลพิษอนุภาคในไอเสียลดลง 18 – 27% และ 16 – 36% เมื่อเปรียบเทียบกับน้ำมันดีเซล   แต่สารประกอบออกไซด์ของไนโตรเจนและอัตราการสิ้นเปลืองเชื้อเพลิงเพิ่มขึ้น 7% และ 5–6% ตามลำดับ การใช้เมทิลเอสเทอร์ของปาล์มสเตียรินและน้ำมันเมล็ดแรพสารมลพิษไอเสียมีปริมาณลดลงทุกชนิดแต่สารประกอบออกไซด์ของไนโตรเจนและอัตราการสิ้นเปลืองเชื้อเพลิงเพิ่มขึ้น

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The effect of biodiesel blended fuels on exhaust emissions of diesel engines was investigated. The test fuels were 2%, 5%, 20% of rapeseed methyl ester, pure rapeseed methyl ester, 2%, 5%, 20% of palm stearin methyl ester, pure palm strearin methyl ester, 20%, 30%, 40% of used cooking oil methyl ester. Two kinds of test vehicles were Toyota D4D 2.5L and Isuzu DMAX 2.5L. The exhaust emissions analysis were carried out by running on chassis dynamometer. The results showed that the blends of 2%, 5% of palm strearin methyl ester and rapeseed methyl ester showed did not significant difference in exhaust emissions and fuel consumption compared to based diesel. In the other hand, the blends of 5% showed tendency reduction of THC and PM emissions. The blends of 20% with all kinds methyl ester, the THC, PM emissions were decreased 10 – 34% and 6 – 34% while the fuel consumption was increased 2 – 5%. Used cooking oil methyl ester blended with diesel in ratio 30, 40 percent were decreased THC, PM emissions 18 – 27% and 16 – 36%. NO_X emissions and fuel consumption were increased 7%, 5 - 6%. Pure palm strearin methyl ester and rapeseed methyl ester provides a greater reduction of all exhaust emissions. On the contrary, NO_X emission and fuel consumption were increased.

Field of study…Petrochemistry and Polymer science…Student’s signature…………
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CHAPTER I

INTRODUCTION

Diesel engines for transportation systems become increasingly popular. However, diesel engine exhaust emissions are major contributor to environmental pollution.

The using of biodiesel fuels for diesel engines seem to emit far less of the most regulated pollutants than standard Diesel fuels. Therefore, vegetable oils represent a promising alternative to conventional diesel fuels. However, several chemical properties of vegetable oils, among them are the high viscosity and high molecular weight, cause poor fuel atomization and low volatility, leading in incomplete combustion and severe engine deposits, injector coking and piston ring sticker. One way to improve the fuel properties of vegetable oil is their transesterification, the products is called “biodiesel”.

According to economic reasons, used cooking oil is also an interesting feedstock for biodiesel production. In fact, Thailand, approximately 17 million liter per year of used cooking. In this sense, transesterification of used cooking oil to produce biodiesel could decrease the waste disposal problem, and reduced dependency on external oil imports, fluctuating energy demands and reduced regulated pollutants.

1.1 Diesel emissions [1]

In the diesel engine, a flammable fuel-air mixture is obtained by injection the fuel at high pressure into high temperature compressed air in the combustion chamber. The fuel self-ignites and the piston is forced downwards producing the woke which is taken from the crackshaft. The use of high compression ratios-typically in the change of 15:1 to 23:1 on automotive diesel engines-ensure that sufficiently high temperature are reached for auto-ignitions to occur.

If the diesel fuel, or indeed any hydrocarbon fuel, were to completely combust in the engine, then just water (H_2O) and carbon dioxide (CO_2) would be form in the exhaust. However, in reality combustion is always incomplete, and a whole cocktail of species are present in the exhaust including unburned hydrocarbon from the fuel and partially oxidized products such as aldehydes and carbon monoxide. Oxides of nitrogen components of diesel exhaust.

Carbon dioxide

Carbon dioxide (CO_2) occurs natually in the atmosphere and is a normal product of combustion. Ideally, combustion of a hydrocarbon fuel should produce only carbon dioxide and water (H_2O). The relative proportion of these two depends on the carbon-to hydrogen ratio in the fuel, about 1:1.75 for ordinary diesel fuel. Thus, an engine's CO_2 emissions can be reduced by reducing the fuel's carbon content per unit energy, or by improving the fuel efficiency of the engine. The high fuel effciency of diesel engines gives them an environmental advantage over some fossil fuels, though the processing of crude oil into diesel fuel has fairly high CO_2 emissions.

Long regarded as benign, the emission of CO_2 from the combustion of fossil fuels has recently attracted considerable attention. Water vapour and CO_2 (along with other gases) allow solar energy to reach the earth. But trap some of the thermal radiation then given off by the earth. This 'greenhouse effect' makes the earth much warmer than it would otherwise be. It is vital to the our climate; we need the greenhouse effect to survive. However, atmospheric levels of CO_2 have been rising since the beginning of the Industrial Revolution.

Carbon monoxide

Carbon monoxide (CO) is toxic. It is an intermediate product in the combustion of a hydrocarbon fuel, so its emission results from incomplete combustion. Emissions of CO are therefore greatly dependent on the air-fuel ratio relative to the stoichiometric proportions. Fuel-rich combustion in variably produces CO, and emissions increase nearly linearly with the deviation from stoichiometric. As diesel engines operate with an overall lean mixture, their CO emissions are normally well below legislated limits and not of much concern. Any CO from a diesel engine is due to incomplete mixing: combustion taking place in locally rich conditions. An oxidation catalyst in the exhaust can further decrease CO and unburnt hydrocarbon emissions. This process is aided by the excess air in the exhaust gas.

Unburnt hydrocarbons

Unburnt hydrocarbon (HC) emissions consist of fuel that is completely unburned or only partially burned. The term HCs means organic compounds in the gaseous state; solid hydrocarbons are part of the particulate matter. The mechanisms leading to HC emissions from diesel engines are completely different from those leading to HC emissions from spark ignition (SI) engines. In the latter, a nearly homogeneous fuel-air mixture is compressed, and then a flame passes across the combustion chanber. Hydrocarbon emissions arise in SI engthes when fuel-air mixture hides out in places inaccessible to this flame. The most significant of these places is the volume between the piston and the cylinder wall, above the top piston ring. In a diesel engine only air is compressed into this volume. In effect, this reduces the air available for combustion, but it does not allow a significant amount of fuel to escape combustion. In a diesel engine, with its non-homogeneous combustion, HC emissions result from problems of fuel and air mixing, and are largely unaffected by the overall air-fuel ratio. There are two primary mechanisms by which fuel escapes the main combustion in a diesel; over-mixed, over-lean regions formed before ignition, and under-mixed fuel injected at low velocity near the end of combustion.

Nitrogen oxides

Nitrogen oxides (NO_x) are comprised of nitric oxide (NO) and nitrogen dioxide (NO_2), with the former making up 70-90% of the total NO_x from diesel engines. Unlike the other pollutants described here, NO_x is a side-effect of combustion, not an incomplete step in it. Burning HC fuel with oxygen powers the engine; atmospheric nitrogen (whih supplies virtually all of the nitrogen in NO_x, fuel-borne nitrogen being negligibly small) is just caught in the reaction process.

The formation of NO is well understood. It is accepted that nitric oxide (NO) is formed by the extended Zeldovich mechanism:

$$O + N_2 = NO + N$$
$$N + O_2 = NO + O$$
$$N + OH = NO + H$$

Nitrogen dioxide (NO_2) forms from NO; quenching by excess air in the cylinder can freeze NO_2 levels at well above equilibrium concentrations.

The formation of NO depends on plentiful oxygen and high temperatures. Gas that burns before the time of peak cylinder pressure is particularly important. After it has burned, it is compressed to a higher pressure and temperature, and so reaches the highest temperature of any portion of the cylinder charge. Thus, the early part of combustion is important for NO_x almost all NO_x is formed in the first 20° of crank angle after the start of combustion. Techniques to control NO_x therefore focus on this stage of combustion. However, most of these techniques reduce combustion temperatures, and so extract penalties in hydrocarbon emission, particulate emissions, and fuel consumption. It is common to refer to the ‘trade-offs between NO_x emissions and particulates and fuel consumption for diesel engines.

Particulates

Particulate matter (PM) is the other diesel emission-along with NO_x-of most concern. It is composed of *soot* (carbonaceous solid matter similar to carbon black), an *extractable fraction* (hydrocarbons extractable with a strong solvent) adsorbed onto the soot, and other contained inorganic compounds (largely sulphates, water and ash). Particulate concentrations and measured by drawing exhaust gas through a filter maintained at 52 °C, and computing the change in filter weight. Because of the methods, there is some overlap between this measurement and both the hydrocarbon measurement and the various smoke measurements. The soot component of the PM corresponds to the smoke measurement, while the extractable fraction corresponds to a portion (ranging from about 25-50%) of the gaseous HC emissions. The exact fraction depends on the engine type and operating conditions, as these affect the distribution of the boiling range of the gaseous HCs emissions.

Presently, oxides of nitrogen (NOx), carbon monoxide (CO), total hydrocarbon (HC), particulates are the emissions which are legislated for diesel engines and their associates health risks, typically associated with diesel engines, lead to the introduction of controls on smoke and particulates.

1.2 Palm oil [17]

The palm oil, Elaseis guineensis, fruit is unusual in that it yields distinct oils: palm kernel oil differs from the kernel and palm oil from the pulp(about 50%). Palm oil is deep orange-red by the large amount of carotene. It is use for making vegetable, margarine, soup, and small amount is used in making thin plate and in aluminium sheet rolling[15].

Palm oil, unlike other vegetable oils, contains equal amount of saturated and unsaturated fatty acids. Crude palm oil is chemically compose of the following:

-50% of saturated fatty acid (Palmitic acid and Strearic acid)

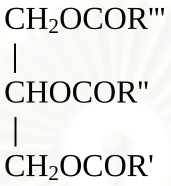
-40% of monounsaturated fatty acid (Oleic acid)

-Vitamin “E” (Tocopherols and Tocotrienols)

-Vitamin “A” (Beta-Carotene)

Fatty acid composition of palm oil

Palm oil has saturated and unsaturated fatty acids which palmitic and oleic acids are the main component acids. More than 85% of unsaturated fatty acids are located at the 2-position of the glycerol nucleus of triglyceride composition of palm oil(Figure). Both the glyceride structure and the FFA content affect the melting and plastic properties of palm oil [15].



$$\begin{array}{l} CH_2OCOR''' \\ \mid \\ CHOCOR'' \\ \mid \\ CH_2OCOR' \end{array}$$

Figure 1.1 Chemical structure of palm oil.

Table 1.1 Composition of fatty acid in palm oil [21].

Fatty Acid Name	No. Of Carbons & Double Bonds	Chemical Structure (= denotes double bond placement)
Caprylic	C8	$CH_3(CH_2)_6COOH$
Capric	C10	$CH_3(CH_2)_8COOH$
Lauric	C12	$CH_3(CH_2)_{10}COOH$
Myristic	C14	$CH_3(CH_2)_{12}COOH$
Palmitic	C16:0	$CH_3(CH_2)_{14}COOH$
Palmitoleic	C16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic	C18:0	$CH_3(CH_2)_{16}COOH$
Oleic	C18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	C18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	C18:3	$CH_3(CH_2)_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic	C20:0	$CH_3(CH_2)_{18}COOH$
Eicosenoic	C20:1	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Behenic	C22:0	$CH_3(CH_2)_{20}COOH$
Eurcic	C22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

Table 1.2 Composition of Fatty acid in palm oil [21].

Fatty acid types	Iodine Value	The main compositions of fatty acids						
		C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Oil palm	14.1-21.0	ND-0.5	0.5-2.0	39.3-47.5	3.5-6.0	36.0-44.0	9.0-12.0	ND-0.5
Palm olean	≥56	0.1-0.5	0.5-1.5	38.0-43.5	3.5-5.0	39.8-46.0	10.0-13.5	ND-0.6
Palm stearine	≤48	0.1-0.5	1.0-2.0	48.0-74.0	3.9-6.0	15.5-36.0	3.0-10.0	0.5
Palm kernal	50.0-55.0	45.0-55.0	14.0-18.0	6.5-10.0	1.0-3.0	12.019.0	1.0-3.5	ND-0.2
Coconut	6.3-10.6	45.1-53.2	16.8-21.0	7.5-10.2	2.0-4.0	5.0-10.0	1.0-2.5	ND
Peanut	86-107	ND-0.1	ND-0.1	8.0-14.0	1.0-4.5	35.0-67.0	13.0-43.0	ND-0.3
Jatropha	101	ND	ND	14.9	6.0	41.2	37.4	ND
Rapeseed oil	94-120	ND	ND-0.2	1.5-6.0	0.5-3.1	8.0-60.0	11.0-23.0	5.0-13.0
Glycine max	124-139	ND-0.1	ND-0.2	8.0-13.5	2.0-5.4	17.7-28.0	49.8-59.0	5.0-11.0

1.3 Used cooking oil

Vegetable oil have been most important role for cooking for long time. Frying by high temperature which most popular for food industry, such as noodle industry, snack industry, beefs industry and fast food. In the present, our country has used cooking oil from food industry very much, about 17 million litres in a years as shown in Table 1-2, Table 1-3. Some of it reused by sale in lower price at the grocery shop. Using used cooking oil for cooking again is effects on health. Because, used cooking oil is heated at high temperature for long time, the structure of used cooking oil's molecules are changed by oxidation, polymerization, cracking reaction, so used cooking oil contains volatility compounds which affect on health and also changed the food tastes. The data from Table 1-1 shown that the peroxide value of used cooking oil much higher than new oil.

Table. 1.3 The average amount of fatty acid in of used cooking oils from fly chicken shop in Bangkok 5 samples.

Types of fatty acid	The amount of fatty acid of new oil (%)	The amount of fatty acid of used cooking oil (%)
Saturated		
Lauric acid (C12:0)	0.45	0.32
Myristic acid (C14:0)	0.38	0.93
Palmitic acid (C16:0)	34.13	38.37
Stearic acid (C18:0)	4.58	4.00
Arachidic acid (C20:0)	0.34	0.34
Total Saturated	40.38	43.97
Unsaturated		
Palmitoleic acid (C16:1)	1.51	0.25
Oleic acid (C18:1)	42.89	45.59
Linoleic acid (C18:2)	14.60	10.03
Linolenic acid (C18:3)	0.62	0.16
Total Unsaturated	59.62	56.03
Peroxide Value (Meq of peroxide oxygen/kg)	2.98	28.08

Table 1.4 Shown a mount of using and used vegetable oil separated by products

Products type	Using vegetable oil		Used vegetable oil	
	(litres/year)	percent	(litres/year)	percent
Bread	19,618,519	23.6	4,770,113	28.9
Snack	4,627,322	5.6	348,978	2.1
Donut	1,297,064	1.6	65,256	0.4
Fried nut	794,579	1.0	701,876	4.3
Fried beef	6,926,863	8.3	3,130,083	19.0
Noodle(Yamyam)	42,602,498	51.2	3,451,850	20.9
Fast food	7,280,980	8.8	4,022,520	24.4
Total	83,147,825	100.0	16,490,676	100.0

Table 1.5 Shown a mount of using and used vegetable oil separated by provinces

Products type	Using vegetable oil		Used vegetable oil	
	(litres/year)	Percent	(litres/year)	percent
BKK	16,558,267	20	5,310,276	32
Perimeter	29,404,612	35	5,778,219	35
Middle	4,923,027	6	1,349,320	8
North	4,265,067	5	510,050	3
North east	1,671,611	2	576,257	3
South	3,737,029	5	876,120	5
East	22,588,212	27	2,090,434	13
Total	83,147,825	100.0	16,490,676	100.0

Using used cooking oil for alternative fuel is reducing the net production of CO_2 from combustion sources and other harmful emissions. In additional, reduced dependency on external oil imports and fluctuating energy demands can be partially subsidized by indigenous renewable fuel. However, used cooking oil has high viscosity and much gum content which effect on engine operation. Therefore, transesterified of used cooking oil is needed. The products from this reaction is called “biodiesel” which its properties like diesel fuel.

Objective and Scope of the Research

The principal objective of this research is to investigate effects of biodiesel blended fuels on exhaust emissions of diesel engines.

In initial study, biodiesel will be prepared from used cooking oil *via* transesterification process using sodium hydroxide as catalyst and then used cooking oil methyl ester was blended with diesel fuel in ratio 2, 5, 10, 20, 30, 40, 50 volume percentage, palm stearin methyl ester and rapeseed methyl ester were blended in ratio 2, 5, 20 volume percent to study effect of biodiesel blended fuel on physical and chemical properties of diesel fuel according to Department of energy business standard and then study effect of biodiesel blended fuels on exhaust emissions of diesel engines.

CHAPTER II

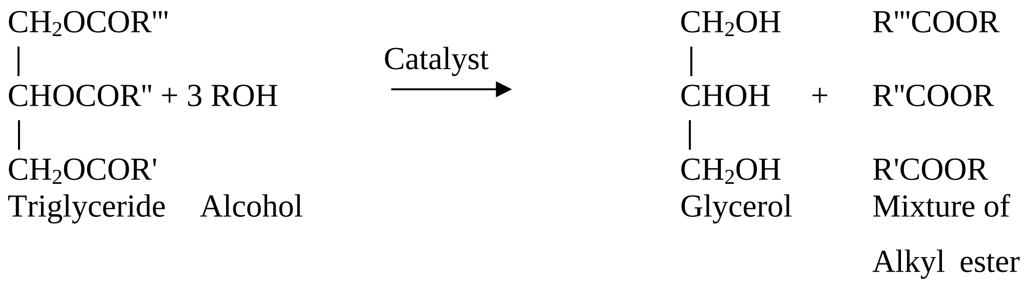
THEORY AND LITERATURE REVIEW

Biodiesel has many advantages over petroleum diesel fuels. Biodiesel fuels is reliable, renewable, and its use can strength the economy by creating jobs, engines running on biodiesel can provide significant emissions reduction benefits for carbon monoxide, particulates, hydrocarbons.

2.1 Transesterification of Vegetable Oils [17]

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed in to another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Figure 2.1). In this review, them transesterification will be used as synonymous for alcoholysis of carboxylic ester, in agreement with most publications this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

In the transesterifation of vegetable oils, a triglyceride reacts with an alcohol in the presence of strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di-and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.



$$\begin{array}{lcll} \mathrm{CH_2OCOR'''} & & \mathrm{CH_2OH} & \mathrm{R'''COOR} \\ | & \text{Catalyst} & | & \\ \mathrm{CHOCOR'' + 3\ ROH} & \xrightarrow{\hspace{2em}} & \mathrm{CHOH}\quad + & \mathrm{R''COOR} \\ | & & | & \\ \mathrm{CH_2OCOR'} & & \mathrm{CH_2OH} & \mathrm{R'COOR} \\ \text{Triglyceride}\quad\text{Alcohol} & & \text{Glycerol} & \text{Mixture of} \\ & & & \text{Alkyl ester} \end{array}$$

Figure 2.1 Transesterifications of vegetable oils.

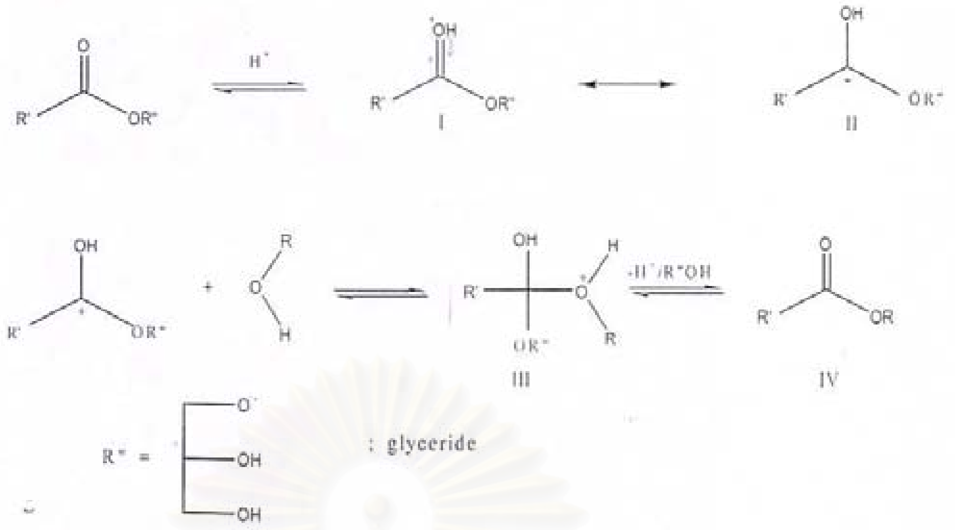
Several aspect, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content, have in influence on the course of the transesterification and will be discussed below, based on the catalyst used.

2.1.1 Acid-Catalyzed Processes

The transesterification process is catalyzed by Bronsted acids, preferably sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically temperatures above 100 °C and more than 3 hours to reach complete conversion.

The alcohol/vegetable oil molar ratio is one of the main factor that influences the transesterification. An excess of the alcohol favors the information of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ration has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetables oils is show in the Figure 2.2, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbonation II which, after a nucleophilic attack of the alcohol, procures the tetrahedral intermediate III, which eliminates glycerol to from the new ester IV, and to regenerate the catalyst H^+.



R’ = carbon chain of the fatty acid
R” = alkyl group of the alcohol

Figure 2.2 Mechanism of the acid-catalyzed transesterification of vegetables oils.

According to this mechanism, carboxylic acids can be formed by the reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterifacation should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.1.2 Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oil is show in Figure 2.3. The first step (Eq.1) is the reaction of the base with the alcohol, giving an alkoxides and the protonated catalyst.

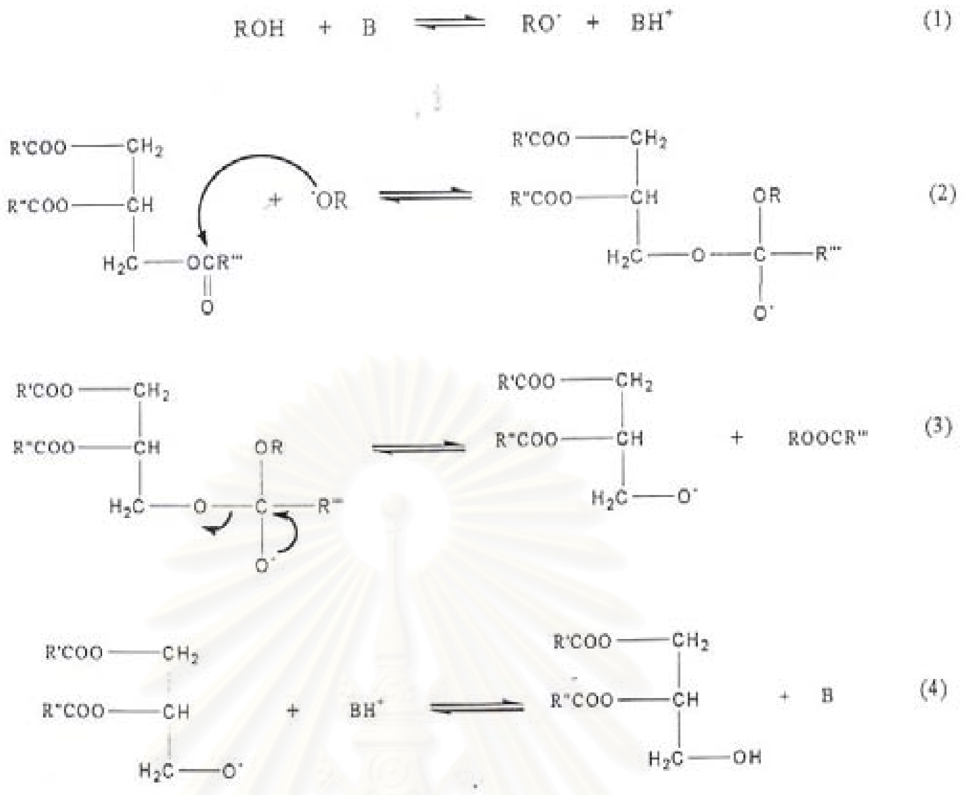


Figure 2.3 Mechanism of the base-catalyzed transesterification of vegetable oils.

The nuecleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq.2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq.3). The latter deprotonates the catalyst, thus regenerating the active species (Eq.4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture if alkyl esters and glycerol.

Alkaline metal oxides (as CH_3ONa for the methanilysis) are the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low concentrations (0.5 mol %). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversion of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol %. However, even if a water-free alcohol/oil mixture is used, some water is produced in the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produce ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably disturbs the recovery of the glycerol due to the formation of emulsions.

Potassium carbonate, used in concentration of 2 or 3 mol %, gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does nor hydrolysis the esters.

2.1.3 Fatty Acid Alkyl Esters as Biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of the next century. Thus, looking for alternative sources of energy is of importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with and energetic content close to diesel fuel. Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel foe diesel engines.

In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol. Different ways have been considered to reduce the high viscosity of vegetable oils:

- dilution of 25 parts of vegetable oil with 75 parts of diesel fuel;
- microemulsion with short chain alcohols (e.g. ethanol or methanol);
- thermal decomposition, which produced alkanes, alkenes, carboxylic acids and aromatic compounds;
- catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes, and
- transesterifition with ethanol or methanol.

Among all these alternatives, the transesterifition seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

Several types of vegetable oils, with a diversified in the fatty acids, can be used for the preparation of biodiesel. Soybean, rapeseed, sunflower and palm oils are most studied. However, there are no technical restrictions to the use of other types of vegetable oils. Consideration the type of the alcohol, the use of methanol is advantageous as it allows the simultaneous separation of glycerol. The same reaction using ethanol is more complicated as it requires a water-free alcohol, as well as an oil with a lower water content, in order to obtain glycerol separation.

Normally, methanol is used as it is the cheapest alcohol in most countries. However, Brazil it is advantageous to use anhydrous ethanol, which is already produced in large quantities to be mixed with gasoline.

2.2 Biodiesel [17]

Biodiesel is a diesel fuel substitute producted from renewable sources such as vegetable oil, animal fat, and recycled cooking oils. Chemically, it is defined as the mono alkyl ethers of long chain fatty acids derived from the renewable liquid sources. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield glycerin and biodiesel (chemically called fatty acid methyl or ethyl esters). Biodiesel can be used in neat form, or blended with petroleum diesel for use in diesel engines. Its physical and chemical properties are similar to petroleum based diesel fuel, non-hazardous and biodegradable as it relates to operation of diesel engines.

2.2.1 Biodiesel’s Attributes

Across the globe environmental concerns and energy security issues have prompted legislation and regulatory actions spurring demand for alternative fuel such as biodiesel. However, the greatest driving force foe the use of biodiesel and biodiesel blends is the need to have a fuel that fulfills all of the environmental and energy security needs previously mentioned which does not sacrifice operating performance.

One of the largest roadblock to the use of altetnative fuel is the change of performace noticed by users. Biodiesel has many positive attributes associated with its use, but by far the most noted attribute highlighted by fleet managers is the similar operating performance to conventional diesel fuel and the lack of change requied in facilities and maintenance procedures. Other attributes and biodiesel and biodiesel blends are detailed below:

2.2.2 Biodegradability

Biodiesel has desirable degradation attributes which male it the fuel of choice by environmentally conscious boaters. Studies at the University of Idaho compared the biodegradation of biodiesel in an aqueous solution to diesel fuel and dextrose (sugar). Biodiesel samples degraded more rapidly than dexstrose, and were 95 percent degraded at the end of 28 days. The diesel fuel was approximately 40 percent degraded after 28 days.

Its should also be noted that blending biodiesel with diesel fuel accelerates its biodegradability. For example blends of 20% biodiesel and 80% diesel fuel degrade twice as fast as No. diesel. Thus, biodiesel use has demonstrated bilodegradability benefits at levels lower than 100%. Simply stated, neat biodiesel degrades as fast as sugar and a B20 bleand will degrade twice as fast as petroleum based diesel fuel.

2.2.3 Flash Point

The flash point of a fuel is defined as the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark of flame. The flash point of biodiesel has been tested and reported by various sources. Specific testing at Southwest Research Institute concluded that the flash point of biodiesel blendes increases as the percentage of biodiesel increases. Therefore pure biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel. Neat biodiesel has a flash point over 300 Fahrenheit, well above the flash point of petroleum based diesel fuel.

2.2.4 Toxicity

The impact on human health is a significant criteria when considering the suitability of a fuel for commercial applications. Health effects can be measured in terms of the fuel’s toxicity to the human body of health impacts due to exhaust emissions. Tests conducted by Wil Research Laboratories, Inc. investigated the acute oral toxicity or pure biodiesel fuel as well as B20, was found to be greater than 5000 mg/kg. The acute dermal toxicity of neat biodiesel was evalutated in a single dose study involving rabbits. The LD_{50} of neat biodiesel was found to be greater than 2000 mg/kg and the 2000 mg/kg dose level was found to be a no observable effect level (NOEL) for systematic toxicity. There were no deaths, remarkable body weight changes or gross necropsy findings for the LD_{50} dose levels for each of the studies.

Acute aquatic toxicity tests with Daphnia Magna have also been conducted. Table salt (NaCl), diesel, and biodiesel were compared to each other. The LC_{50} count (the concentration where 50 percent of the daphnia Magna have died and 50 percent were still alive) for table salt was 3.7 parts per million (ppm), 1.43 ppm for diesel fuel, and 23-332 ppm for biodiesel. Therefore, biodiesel is less toxic than diesel fuel and table salt.

2.2.5 Emission Reductions

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods employed.

The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to CO_2), eliminates the sulfate fraction (as there is no sulfur in the fuel), while the soluble, or hydrocarbon, fraction stays the same or is increased. Therefore, biodiesel works well with new technologies such as catalysts (which reduces the soluble fraction of diesel particulate but not the solid carbon fraction), particulate traps, and exhaust gas recirculation.

2.2.6 Health Effects

Evidence does exist which indicates that diesel particulate matter is a potential carcinogen. In 1988, the National Institute for Occupational Safety and Health (NIOSH) recommended that whole diesel exhaust be regarded as “a potential occupational carcinogen,” as defined in the Cancer Policy of the occupational Safety and Health Administration. The use of biodiesel decreases most regulated emissions. Research results indicate that particulate matter (specifically the carbon or insoluble fraction), hydrocarbons, and carbon monoxide are significantly reduced.

In addition to reducing the overall levels of pollutants and carbon, the compounds that are prevalent in biodiesel and diesel fuel exhaust are different. Research conducted by Southwest Research Institute on a Cummins N14 engine indicates that biodiesel exhaust has a less harmful impact on human health than petrodiesel. Biodiesel emissions have decreased levels of all target polycyclic aromatic hydrocarbons (PAHs) and nitrited PAHs compounds, as compared to petroleum diesel exhaust. PAHs and nPAHs compounds have been identified as potential cancer causing compounds. All of the PAH compounds were reduced by 75 to 85 percent, with the exception of benzo(a)anthracene, which was reduced by roughly 50 percent. The target nPAH compounds were also reduced dramatically with biodiesel fuel, with 2-nitrofluorene and 1-nitropyrene reduced by 90 percent, and the rest of the nPAH compounds reduced to only trace levels. All of these reductions are due to the fact the biodiesel fuel contains no aromatic compounds of any kind, including PAHs.

In addition, the total speciated hydrocarbon mass of biodiesel is nearly 50 percent less than that measured for conventional diesel fuel, and the associated ozone potential is reduced by the same amount. Sighificant reductions in most aldehyde compounds were also observed with biodiesel, with formaldehyde and acetaldehyde 30 percent lower than the levels observed for conventional diesel fuel.

2.2.7 Lubricity

In the United States the sulfur level of diesel fuel that is used for on-road purposes is limited to 0.05% by weight. This limit was mandated in October 1993 as a method to decrease particulate matter emitted from diesel powered vehicles. With the introduction of mandated Environmental Protection Agency (EPA) low-sulfur diesel fuel, fleet operators began to encounter premature wear and/or failure of injector pumps in increasing numbers. Pump manufacturers such as Stanadyne and Bosch began recommending the use of lubricity additives to alleviate the serious damage that the reduced sulphur content of low sulfur diesel was causing to their injection pumps.

Many petroleum distributors are only marketing low-sulfur diesel even though it remains legal to sell high-sulfur diesel in off-road markets. Testing at labs such as Southwest Research Institute, Stanadyne Automotive, and Engineering Testing Services have demonstrated that biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using the High Frequency Reciprocating Rig test indicate that there is a marked improvements in lubricity when biodiesel is added to conventional diesel fuel, even at blend levels below 1%.

2.2.8 Stability [21]

Oxidative stability is major industry issue for diesel and biodiesel fuels. Some biodiesel are more stable others and unstable biodiesel contain stability additives that perform very well. The tendency of a fuel to be unstable can be predicted by the Iodine number (ASTM D 1510) but the test method may not pick up the presence of stability additives. Iodine number actually measure the presence of C=C bonds that are prone to oxidation. The general rule of thumb is that instability increases by a factor of 1 for every C=C bond on the fatty acid chain; thus 18:3 are three times more reactive than 18:0. Stability can be predicted from knowledge of feedstock only if you know the proportion of C18:2 and C18:3 fatty acids present in the fuel and know whether or not the fuel has been treated for stability. High fractions of those two types of fatty acids can adversely affect fuel stability if additives are not used.

Poor stability can be lead to increasingly high acid numbers, increasing viscosity, and formation of gums and sediment that can clog filters. Long – term storage in the presence of diesel fuel, diesel additive, water, sediments, heat, and air has not been adequately documented in the field. Biodiesel and blends of biodiesel and diesel fuel should not be store for longer than 6 months either storage tanks or vehicles until better field data is available.

2.2.9 Infrastructure

In general, the standard storage and handling procedure used for petroleum diesel can be used for biodiesel. The fuel should be stored in a clean, dry, dark environment. Temperature extremes should be avoided. Acceptable storage tank materials include stainless steel, fluorinated polyethylene, and fluorinated polypropylene. Biodiesel has a solvent effect which may release deposits accumulated on tank walls and pipes from previous fuel storage. The release of deposits may clog filters initially and precautions should be taken.

2.3 Properties of Diesel Fuels [7]

Although diesel engines vary widely in size, power, speed output, and mechanical design, their fuel requirement are quite similar in many respects. Performance features desired of all diesel fuels, and physical properties most directly related to them are summarized below. Fuels properties are presented in the order in which they are seen by the engine as the fuel flows from the storage tank, through the fuel system, to the combustion chamber. No attempt is made in the table to indicate relative importance.

Performance Feature Desired	Indicated By
1. Safety in handling	Flash point
2. Pumpability at low temperature	Pour or cloud point, Viscosity
3. Freedom from all suspended matter	Storage stability
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane No.
6. Clean burning	Volatility, Cetane No.
7. Good fuel economy	API Gravity
8. Major effect on engine wear and deposits	Sulfur, Aromatics

Except for the calorific value or energy content, the required properties of hydrocarbon in fuels for diesel engines differ significantly from those in gasoline engines. Cetane number, density, viscosity, low-temperature property, sulfur content, aromatic content, volatility and boiling range make up the essential characteristics of diesel fuels necessary for satisfactory operation of the diesel engine.

2.3.1 Cetane number (CN). is a measure ignition quality or ignition delay , and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. A high cetane number is representative of a short ignition delay. This properties is related to the fuel composition. The two standards, cetane (n-hexadecane) and 1-methylnaphthalene (1-MN) are assigned CN value of 100 and 0, respectively. The operating definition of CN represents the volume percentage of cetane which must be mixed with 1-MN to give the same ignition performance as s given real diesel fuel. Due to the difficulty to obtain large supplied of pure 1-MN (partly due to oxidative degradation during storage), there is now a secondary standard in use, heptamethylnonane (2, 2, 4, 4, 6, 8, 8-heptamethylnonane), which is assigned a CN = 15, and the corresponding equation for CN is as follows:

$$CN = \text{vol.\% of cetane} + 0.15\ (\text{vol\% of heptamethylnonane})$$

The auto-ignition phenomenon is the basis of the physical meaning for cetane number. In the compression stroke, the air is precompressed until its temperature exceeds that necessary for auto-ignition or spontaneous combustion of the fuel. Near the end of compression stroke, the diesel fuel is injected into the cylinder in atomized form and is vaporized in the air. Auto-ignition temperature (AIT) is defined as the lowest temperature at which a substance will ignite in the absence of a spark of flame. Auto-ignition is initiated at elevated temperature where the oxygen in the air can begin to interact with the hydrocarbon, the resulting in an exothermic oxidation reaction. When the rate of heat production exceeds the rate at which the heat can be dissipated to the surrounding, auto-ignition occurs. Auto –ignition is believed to proceed through a free radical mechanism. The ease of auto-ignition generally increases, and thus AIT decrease in the order of aromatics< branched alkanes< cycloalkanes<n-alkane

2.3.2 Cetane Index (CI). Cetane index is a calculated value, derived from fuel density (see below) and volatility. Cetane index usually gives a reasonably close approximation to real cetane number, which is derived from measurement in a rail engine. Cetane index is wildly used for routine monitoring of diesel fuel ignition quality. The calculated cetane index has mainly served as an alternative method of determining the ignition quality of diesel fuel to minimize the need for engine tests. The method D4737-1998 by ASTM (American society for Testing and Materials) gives the relatively new equation for calculating the cetane index that used density and three distillation points are shown below:

$$CI = 45.2 + 0.0892(T_{10} - 215) + 0.131\ (T_{50} - 260) + 0.0523\ (T_{90} - 310) + 0.901\ B(T_{50} - 260) - 0.420\ B(T_{90} - 310) + 0.0049\ (T_{10} - 215)^2 - 0.0049\ (T_{90} - 310)^2\ 107.0\ B + 60.0\ B^2$$

Where T10, T50 and T90 are the 10%, 50%, and 90% recovery temperatures in °C. respectively, according to the distillation curve, correct to standard barometric pressure, and D the dendity in kg/l at 15 °C and

$$B = e^{[-3.5(D-0.85)]} - 1$$

2.3.3 Heating value. Heating value is defined as the amount of heat released per unit mass of fuel from its complete combustion. This property is also referred to as calorific value or energy content. Although cetane number determines the combustion performance, it is the heating value along with thermodynamic criteria that sets the maximum possible output of power. Heating value can be measure by ASTM D4809 method for transportation diesel fuels and by ASTM D 4868 for plant diesel fuels. Typical heating values for diesel fuels are in the range of 134,000 Btu/gal (19,700 Btu/lb) to 148,000 Btu/gal.

2.3.4 Density. Density is the mass per unit volume of diesel at given temperature. It can provide useful indication about a fuel's composition and performance-related characteristics. Density has an importance in diesel engine performance, since fuel injection operates on a volume metering system. A change in density will influence engine output due to different mass of fuel injected, and a higher density fuel will tend to produce more smoke as well as more power. The densities of fuels obtained by different refining processes are approximately as follows:

Straight-run distillates	0.805-0.870 g/ml
Hydrocracked gas oil	0.815-0.840 g/ml
Thermally cracked gas oil	0.835-0.870 g/ml
Catalytically cracked gas oil	0.930-0.965 g/ml

A limit to maximum density is set to avoid smoke formation at full load. Therefore, the density of diesel fuels should be in the range of 0.80-0.86 g/ml (800-860 kg/m^3). A related unit is API gravity by the American Petroleum institute.

$$\text{API gravity } (°) = [141.5/(\text{specific gravity at } 60\ °F(15.6\ °C))] - 131.5$$

It may be note that water has a specific gravity of 1.0 g/ml an API gravity of 10.0°. API gravity is a useful measure of density for liquids lighter than water. Diesel fuels have API gravity of 33-45°. Density differs from API gravity in that the higher the number in degree API, the lighter is the fuel.

2.3.5 Viscosity. Viscosity is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion. It reflects on the extent of intermolecular (attractive) forces and decreases with increasing temperature. Therefore, the viscosity of a fluid indicates its resistance to flow; the higher the viscosity , the greater the resistance to flow. The viscosity of diesel fuels is important for fuel flow and engine operation. The unit of viscosity is the poise, which is the force required to move an area of 1 cm^2 at a speed of 1 cm/sec past two parallel surfaces that are separated by the fluid. The kinematic viscosity is the ratio of the viscosity to the density. The unit of kinematic viscosity is the Stoke (St), measured in cm^2/s but often reported in centistokes (cSt).

For convenience, the two figures as often expressed in centipoises (cP) and centistokes (cSt), and the two are related in that cP = cSt x density of the liquid. The term centistokes is being replaced by the preferred SI (System International) unit mm^2/s. A widely used laboratory method for determining the kinematic viscosity of diesel fuels is ASTM D445, which measures the time taken for a fixed volume of the fuel to flow under gravity through a capillary tube viscometer immersed in a thermostatically controlled bath.

Viscosity is an important property of diesel fuel because of its relevance to the performance of the fuel injection equipment, particularly at low temperature when the increase in viscosity affects the fluidity of the fuel. Increasing viscosity reduces the injector spay cone angle and fuel distribution and penetration while increasing the droplet size.

If viscosity is too high, poor atomization of fuel spray results, which leads to poor combustion and loss of power, and thus poor fuel economy. If the viscosity is too low, the lack of lubricity leads to injector pump wear. Very low viscosity can also result in significant leakage of fuel from pumping elements, particularly at low pumping speeds.

2.3.6 Boiling Range. Boiling range is defined by the initial boiling point (IBP) and final boiling point (FBP) in the distillation curve. Most diesel fuels contain hydrocarbon with boiling points within the range of 150 to 380 °C. For typical transportation diesel fuels in the U.S., boiling range is between 177 °C (350 °F) to 343 °C (650 °F).

2.3.7 Distillation Curve. It is necessary to obtain values for T10,T50, and T90 to meet fuel specification and to calculate the cetane index. The development of simulated distillation gas chromatography (Sim Dis Gc) has resulted in a never and simpler method for determining the distillation cure in addition to the boiling rage of the hydrocarbon fuels. AST M D2887 method can be used for measuring the boiling rage of diesel duels with GC. ASTM D 2887 method is much more efficient than the old distillation method ASTM D86. SimDis GC can be used for evaluating boiling rang of light oils, heavy oils and even residual oils and their upgrading products. SimDis GC method generally uses a non-polar stationary phase (such as polymethylsiloxane) for GC column where the compounds are separated base on their different in boiling points. Thus the retention times of fuel components give their equivalent boiling points after calibration with standards. Fuels oils used for low- and medium-speed engines have more higher boiling components that uses to require high- temp of vacuum distillation for analysis, but they all can be easily analyzed now by using 1 µl injection of the sample into SimDis GC. The extent of deviation from true boiling points depends on the contents of different compound classes in fuels as well as the polarity of GC column .

2.3.8 Volatility. Volatility of the fuel influences many other properties including density, auto-ignition temperature, cold-ignition temperature, flash point, viscosity, and cetane number. Volatility depends on the boiling range and the content of light fractions, which can be measures by distillation with SimDis GC. Increasing the contents of lower boiling fractions increases the volatility of fuels.

2.3.9 Flash point. Flash point is the temperature to which fuel must be heated to produced a vapor-air mixture (above the liquid) that will ignite and spread over the liquid surface when a small flame is applied. It can be measured by ASTM D93 method using a Pensky-Martens closed cup tester, where the lowest temperature at which a small flame of a specified size causes the vapor above the sample to ignite and be self sustaining is recorded as the flash point. Flash point is roughly proportional to boiling range and volatility, and relates to the front-end volatility of the fuel. Typical minimum values of flash points for automotive diesel fuels range from 38-52 °C in the U.S. to 56 in some European counties. As far as performance in an engine is concerned, the flash point of a diesel fuel has no significance. It is solely concerned with fuel storage safety.

2.3.10 Pour point. Pour point is the temperature at which the amount of wax precipitated out of the solution is sufficient to gel the fuel. It is the lowest temperature at which the fuel is observed to flow. Definition from ASTM is the temperature at which a measured volume of fluid does not flow for 5 seconds when tilted horizontally. It is usually the lowest temperature at which a fuel can be pumped. The pour point is generally 5-11°C below could point. No wax precipitation problems are encountered above the cloud point. Pour points for most automotive diesel fuels are usually between -15 and -35 °C.

2.3.11 Cloud point. Cloud point is the temperature a which wax is first precipitated, thus fuel begins to appear “cloudy”. By the ASTM method D2500, it is the temperature at which wax first becomes visible to the observer when the fuel is cooled in a glass vessel at a specified rate. Cloud point depends on boiling range and paraffin content of fuel. Heavy n – alkanes are first components to come out as wax. Unfortunately the better the ignition quality of the fuel components, the less desirable their low temperature propertied are. One of the drawbacks of cloud point measurement is its dependence on the tester’s judgment. Usually the cloud point of diesel is in the range between 10 and -20 °C depending upon location and season.

2.3.12 Low – Temperature Filterability. Cold filter plugging point (CFPP) is the lowest temperature at which a given volume of diesel fuel passes through a well defined filter in a limited time interval. By European standard method EN116, this is the lowest temperature at which 20 ml of fuel will pass through a 45 um fine wire mesh screen in less than 60 seconds. However, CFPP does not correlate well with vehicle performance in the US where the fuel blends, quality, and weather conditions are different. Consequently, the low – temperature flow test (LTFT) has been developed in the U.S. as ASTM D4539. it differs from the European CFPP test in that it requires a fixed volume of fuel to be cooled and filtered through a 17 um mesh screen. The LTFT pass temperature is the lowest point at which a fixed volume of fuel (180 mL) of fuel passes through the screen in less than 60 sec.

The cloud point is the highest temperature used for characterizing cold flow, and the pour point is the lowest. The CFPP and LTFT temperatures will be somewhere between the cloud and pour points.

2.3.13 Stability. storage stability can be an issue for diesel fuels. Some insoluble materials can be formed to oxidative degradation of fuel during storage. Excessive amounts of insoluble material can clog the screen and engine filters and cause malfunction. ASTM D4625 method measures the quantity insoluble material formed during storage of diesel fuels under air over periods of 0, 4, 8, 12, 18, and 24 weeks. This method is not suitable for quality control testing because of long storage periods. There are two accelerated oxidation tests adopted by ASTM. In ASTM D2274, a fixed volume of fuel is bubbled with oxygen for a given period of time at a specific rate and temperature. The total amount of filterable and adhesive insoluble formed during the test are measured as mg per 100 mL. ASTM D5304 uses oxygen overpressure (100 psig) for a fixed volume of fuel (100 mL), without or with stabilizer additives, placed in a borosilicate container that is placed inside a pressure vessel at 90 °C for 16 hours. At the end of the test, the sample is cooled and the amount of insoluble determined. This method achieves acceleration of oxidation without resorting to higher temperature.

2.3.14 Color. Color is another property of diesel fuel. It is viewed as a qualitative indication of diesel fuel quality. By ASTM D1500 test, which employs a standard light source and a comparison of colored glass disks, a scale ranging from 0.5 to 8.0 is used. A variation outside the established range may indicate degradation or contamination of the fuel with other products. Some hydrotreated light oils also have color, but they can be rendered colorless by a low – temperature hydrogenation.

2.3.15 Diesel Index. is also used to represent the quality of diesel fuels. Diesel index can be derived from API gravity and aniline point, but the result can be misleading, especially when applied to blended fuels. To determine aniline point, a specific volume of aniline is mixed with the fuel, as described in the ASTM D611 method. The mixture is cooled at controlled rate. The temperature at which two phases separate is defined as aniline point. Aniline points are high for paraffins and low for aromatics, with cycloalkanes and olefins in between; aniline number has been found to correlate with cetane number of diesel fuels. Aniline point could be used to estimate aromatics content of a fuel, but the quantitative determination method.

2.4 Composition of Diesel Fuels [7]

2.4.1 Type of diesel fuels

Compositions of fuels for diesel engines are generally different from those for gasoline and jet engine, as seen from Table 2.1

Table 2.1 Comparison of diesel fuels with gasoline and jet fuels.

Fuel	Distillation Fraction	Boiling Range, °C	Sulfur Wt%	Engine for Use[a]	Quality Indicator
Gasoline	Gasoline	30 – 225	0.035	S.I.	Octane No.
Jet Fuel	Kerosene	160 – 300	0.1-0.4	Gas Turbine	Specs
Diesel	L Gas Oil	160 – 380	0.035	C.I.	Cetane No.

a): SI: spark ignition; CI: compression ignition; Specs: specifications.

There are three classes of diesel engines, those for high-speed diesels-trucks, cars, locomotive; those for medium-speed diesel-marine auxiliaries, stationary power generators, and those for low speed diesels (marine diesel) – ships, fishing boats, farm tractors, and electric power generators. The fuels for high-speed diesel engines can operate on fairly – poor quality fuel such as marine diesel, heavy fuel oil and heating oil. In some cases they can even operate on crude oils. Typical ranges of diesel engines are listed below:

Table 2.2 Typical ranges of diesel engines.

Type	Range	Conditions and applications
High Speed	>1000 rpm	Frequent variation in load and speed Road transportation vehicles Diesel locomotives; construction equipment
Medium Speed	300 – 1000 rpm	Fairly high load, relatively constant speed Marine auxiliary; Pumping units Stationary power generation
Low Speed	<300 rpm	Heavy load, constant speed; Marine main propulsion; Electric power generation

There are several types of diesel fuels specified in the U.S. ASTM D976-04 (No. 1 – D , No.2 – D , and No. 4 – D diesel fuels is generally made from virgin or hydrocracked stocked having cetane numbers above 45. It is a relatively volatile distillate fuel oil for engine requiring frequent speed and load change. It has a narrow boiling range of 182 to 316 °C (maximum T_{90}: 288 °C) and is used in high – speed engines in automobiles, trucks, and buses. Such fuel require for used at very low temperatures. No.2 – D diesel fuel has a wide boiling range and lower volatility than No. 1 – D, and it is similar to No. 2 – D fuel oil. It is usually contains cracked stocks and may me be blended from naphtha, kerosene, and light cracked oil from the coker and the fluid catalytic cracking unit. No 2 – D fuels are transportation diesel fuels. They are used for applications that do not require a high-volatility fuels. They can also be used for engines in industrial and heavy mobile services. The specification for No. 1 – D diesel fuel overlaps with kerosene and jet fuel, and all three are commonly produce from the base stock. One major use of No. 1 – D diesel fuel is to blend with 2 – D during winter (in cold regions) to provide improved cold flow properties. No. 4 – D diesel fuels are generally low – quality fuels for low – and medium – speed engines in non – automotive application. The focus of this article is automotive diesel fuels.

The heating value for 1 – D, 2 – D, and 4 – D diesel fuels are around 134,000, 138,000 and 148,000 Btu/gal, respectively[]. In addition, No. 2 – D diesel fuel is similar to No. 2 fuel oil which is made from blended naphtha, kerosene, diesel and cracked gas oils. No. 2 fuel oil may have higher final boiling point (FBP) than No. 2 - D. Similarly, No. 4 – D diesel fuel and No. 4 fuel oil have similar specifications.

Railroad diesel fuels also have market worldwide. For example, there are approximately 25000 diesel locomotives in the U.S. alone. Railroad diesel fuels are generally similar to the heavier automotive diesel fuels but they have higher boiling range up to 400 °C and lower cetane numbers (30 minimum)

Military diesel fuels are generally lighter fuels; they typically consist of distillate fractions having narrow boiling range with more lower boiling components than commercial automotive diesel fuels for high – speed diesel engines.

2.4.2 Molecular Components of Diesel Fuels

The compound classes and molecular components of diesel fuels are described below. Diesel fuels consist mainly of saturate (paraffins and naphthenes) and aromatic hydrocarbons. Their relative distribution depends on the feedstocks and fuel processing schemes. It should be noted that refineries of oil companies generally very the mix of hydrocarbons in the fuels they supply to suit the demand, climate and the season of the year. The include more components of low boiling range in cold climates and in winter, and vice versa in hot weather.

2.4.3 Saturate Hydrocarbons

Generally, long – chain alkanes with carbon numbers in the range of C_{10} – C_{20} are the major paraffinic components. The corresponding lower and upper boiling points for the n – alkanes are 174 °C (n – C_{10}) and 344 °C (n – C_{20}), respectively. The boiling range in the distillation curve of a diesel fuels cloud cover the range from about 160 to 380 °C. there can be some lighter (C_{9-}) and heaver (C_{20+}) components, but they exist in small quantities in most high – way diesel fuels.

The components of heavier components in fuel oils for low – speed diesel engines are higher than those in automotive diesel fuels. Long – chain paraffins have excellent cetane numbers and show good combustion performance, but higher – boiling n – alkanes tend to have higher cloud points and do not have good cold – flow properties.

Alkylated cycloalkanes are also present in diesel fuels. Alkylcyclohexanes, decahydronaphthalenes and perhydrophenanthrenes are typical examples of one to three ring cyclohexanes in diesel fuels, and in hydrotreated ligh cycle oil. The contents of naphthenic components depend on both the nature of the crude and the blending stocks as well as processing parameters.

2.4.4 Aromatic Components

While aromatic compounds can be identified by GC – MS (gas chromatograph coupled with mass spectrometer), the contents of aromatic and saturate compounds in diesel fuels can also be quantitatively determined by HPLC (high – performance liquid chromatograph). The aromatic compounds can be separated into monoaromatics, diaromatisc, and polyaromatics by HPLC with a refraction index detector using amino column made with the silica gel modified by NH_2 groups. Alternatively, a tetrachlorophthalimidopropyl bonded silica as the normal – phase column with photo diode array detector can be used.

The aromatic compounds in diesel fuels include alkylated benzenes, indanes , naphthalenes, tetralins, biphenyls, acenaphthenes, phenanthrenes, chysenes, and pyrenes. Diaromatic hydrocarbons with naphthalene – type structure are more abundant aromatic components in diesel fuels.

Straight – run gas oils (SRGO) or middle distillates generally have between 20 to 35 wt% aromatics while light cycle oil (LCO) from fluid catalytic cracking (FCC) may contain from 50 to 80 wt% aromatics that can be determined by HPLC, with the following distribution:

Aromatics in SRGO	20 – 35 wt%
Monoaromatics	15 – 35 wt%
Diaromatics	5 – 35 wt%
Polyaromatics	0 – 5 wt%

Aromatics in LCO	50 – 80 wt%
Monoaromatics	10 – 35 wt%
Diaromatics	30 – 50 wt%
Polyaromatics	5 – 15 wt%

Retention indices for temperature – programmed GC and GC – MS analysis of aromatic and saturate as well as polar compounds in hydrocarbon fuels have been determined for over 150 compounds. The indices for different compound classes respond to the changes in GC column temperatures in a different fashion, which can also be used to identify different compounds and distinguish different isomer s, as has been demonstrated for petroleum derived and coal – derived middle distillates.

2.4.5 Sulfur Content

Sulfur content is usually expressed as the weight percentage of sulfur in the fuel, because there are many different sulfur – content compounds in petroleum – derived fuels. Sulfur content in diesel fuel is an environmental concern because, upon combustion, sulfur is converted to SO_X (SO_2 and SO_3) during combustion which poisons the catalytic converter for exhaust emission treatment and also contributes to acid rain. In general, high sulfur content is highly undesirable for several reason:

- Sulfur compounds contaminate lubricants
- SO_X emission
- SO_X poisons catalysts for emission treatments
- SO_X corrodes engine cylinder, exhaust system
- Increases corbon deposits in cylinders and on pistons
- Increase mass of particulate (sulfate aerosols)

The maximum sulfur content of automotive diesel fuels in the U.S. was reduced by regulations from about 0.26 – 0.50 wt % to 0.05wt%. on October 1, 1993 for all automotive diesel. The sulfur content of diesel fuel in Europe was limited to 0.3 w% in 1989 to 0.2 wt% in 1994, and further reduced to 0.05 wt% from October 1, 1996. Thus diesel sulfur content in Japan was reduced by regulation from 0.4 wt% to ≤ 0.2 wt% in 1993, and further to ≤ 0.05 wt% in 1997.

Currently the fuels specifications of all automotive diesel fuels in the Thailand limit the sulfur content of diesel fuels to be less than 0.035 wt% or 350 parts per million by weight (ppmw). The new regulations by the US EPA will future lower the contents of sulfur and aromatics, with diesel sulfur content further reduced to 50 ppmw from the current content 500 ppmw.

2.4.6 Heteroatom – Containing Compounds

Due to higher boiling range, the sulfur compounds in diesel fuels have higher molecular weights and larger ring sizes than the sulfur compounds in gasoline. Typical feedstocks for making diesel fuels in the U.S. include straight – run gas oil, LCO from FCC, vacuum gas oil, coker distillates, and visbreaker distillates; their sulfur contents may range from 0.4 wt% to 2.4 wt%. Most sulfur compounds are alkylated benzothiophene – type and dibenzothiophene – type species in diesel fuels, as compared to thiophene – type and some benzothiophene – type cyclic sulfur species in gasoline.

Kabe and coworkers analyzed the sulfur compounds in light gas oil and hydrotreated gas oils using gas – chromatography with an atomic emission detector (GC – AED) and GC – mass spectrometry (GC – MS). Forty two alkylated benzothiophene compounds and twenty nine alkylated dibenzothiophene compounds were identified. Among them the 4,6 – dimethyl dibenzothiophene was found to remain even after deep hydrodesulfurization.

Ma et at analyse polycyclic sulfur compounds in a non – polar fraction of fraction of vacuum gas oil. Hsu and coworkers performed mass spectrometric analysis of many diesel fuels and petroleum fractions. The major compounds in all classes and trace amount of heteroatom – containing compounds were found.

Trace amounts of nitrogen compounds in diesel fuels includes, carbazole, quinolines, acridines, and phenanthridines. The oxygen compounds are alkylated phenols and dibenzofurans. Formulated diesel fuels also contain trace amounts of additive.

2.5 Diesel engine [17]

Type diesel engines and gasoline engines are reciprocating engines that operate with four stroke of the piston in the cylinder:

1) Induction (intake)
2) Compression
3) Power (ignition and expression)
4) Exhaust

The gasoline engines draw in a pre- mixed combustible charge of air and fuel, whereas the diesel unit is supplied with air and fuel separately. Power control over gasoline engine is effected by throttling the flow of the air/fuel mixture into the injected per induction stroke into the cylinders.

Specifically, the diesel engine takes in and compresses air. The air compression increases the pressure and temperature inside the cylinder to values in the rage of 3-5 MPA and 500-600 ˚C, respectively. Shortly before the end of the of the compression stroke, one or more of fuel are injected into the cylinder. The fuel droplets absorb heat from the compressed air and vaporize, and then ignition of the fuel begins by auto-ignition in one or several zones in the marginal operating conditions such as cold starting, a high compression ratio is necessary, generally between 14 and 25. The delay time between injection (vaporization) and ignition must be kept short. If the ignition delay of the large quantity of fuel can causes diesel knock, which is noisy and can cause damage to the engine.

In a high-speed diesel engine, the delay time between fuel ignition and ignition is only about 0.5-0.6 ms. After ignition, fuel ignition continues for a portion of the power stroke; the addition fuel burns as a diffusion flame (almost instantly) as it mixed with the remaining air and combustion products in the cylinder. Fuel injection is terminated partway through the power stroke. The rate of injection is carefully controlled during fuel injection to provide smooth engine operation. The temperature and pressures of gases inside cylinder of diesel engines during combustion can reach as high as 1600-2000 ˚C. Power output is controlled, not by adjusting the quantity of air/fuel mixture as in the case of spark ignition engines, but by changing the mass (flow) of diesel fuel introduced into a fixed volume of air.

By the concept, the diesel engine operates at variable fuel-air ratios. It is not possible to attain the stiochiometric ratio because the fuel does not diffuse in an ideal manner into the air. A large part of combustion occurs (after the auto-ignition) in a diffusion-type flame. The equivalence ratio is defined as the actual fuel-air ratio divided by the stoichiometric fuel air ratio. For an average equivalence fuel-air ratio of 1.00, the combustion accompanied by smoke and soot formation. Finally, at full load, the overall equivalence ratio in a diesel engine is between 0.7 and 0.85.

For the gasoline engine, auto-ignition is highly undesirable and is minimized as much as possible by design and by fuel formation, to avoid engine nock. It seems surprising at first glance that auto-ignition should be so highly desirable and preferred in the diesel engine. This is because auto-ignition in diesel engine occurs in very localized zones and concerns only a small fraction of the total amount of fuel introduced. Thus there are one or more ignition centers instead of auto-ignition of one massive homogeneous system which characterizes knocking. Furthermore, the study the structure of the diesel engine provides good residence to damage which might be caused by a rapid release of energy at the moment of auto-ignition.

2.6 The Diesel Combustion Process [7]

The diesel combustion process in diesel engines is a complex sequence of events consisting of 3 phases. *The first phase* is the ignition delay period during which the fuel must vaporize, mix with air, and undergo pre-flame chemical reaction that produce the chemical species necessary for spontaneous combustion. *The second* is the premixed burning phase (chemically controlled), which is spontaneous combustion regions of fuel-air mixtures formed (prepared) during the ignition delay period. The rapidly rising temperature and pressure in the cylinder accelerate the combustion in an uncontrolled manner until the backlog is depleted. *The third phase* is the diffusion burning phase (controlled by mixing rate). After the second phase, the fuel in the spray core is too rich to burn, and the fuel in the periphery of the spray is too burn. As a result, combustion slows down and is controlled by the rate at which the air is entrained and a combustible mixtures formed.

The rate of burning during the mixing-controlled phase depend on the air motion and fuel spray momentum. The burning rates starts quite high because there is considerable excess air and the fuel spray entrain air rapidly. After the end of ignition, particularly at high loads when there is not as much excess air as with light loads, the burning rates decrease gradually.

2.7 Combustion of Diesel Fuel Oils [7]

Both physical and chemical processes are involved to any combustion process. In the diesel engine, the physical processes include transportation of the fuel and air into the combustion chamber, mixing of fuel and air, and provision of environmental conditions favorable to chemical reaction. The chemical process involve self-ignition or auto-ignition of the fuel and finally extensive chemical reaction that liberates the potential energy in the fuel.

2.8 Combustion Type of Diesel Engines

Diesel engines are durable and efficient. Most of the diesel engines in commercial vehicles are direct injection (DI) engines and indirect injection (IDI) which each type of engine are describe:

2.8.1 Direct injection (DI) systems [10]

In the large – size engines, where mixing rate requirements are least stringent, quiescent direct – injection systems of the type shown in Fig 2.4 are used. The momentum and energy of the injected fuel jets are sufficient to achieve adequate fuel distribution and rates of mixing with the air. Additional organized air motion is not required. The combustion chamber shape is usually a shallow bowl in the crow of the piston, and a center multihole injector is used.

As engine size decreases, increasing amount of air are used to achieve faster fuel – air mixing rates. Air swirl is generated by suitable design of the inlet port, the swirl rate can be increase as the piston approaches TC by forcing the air toward the cylinder axis, into a bowl- in – piston type of combustion chamber

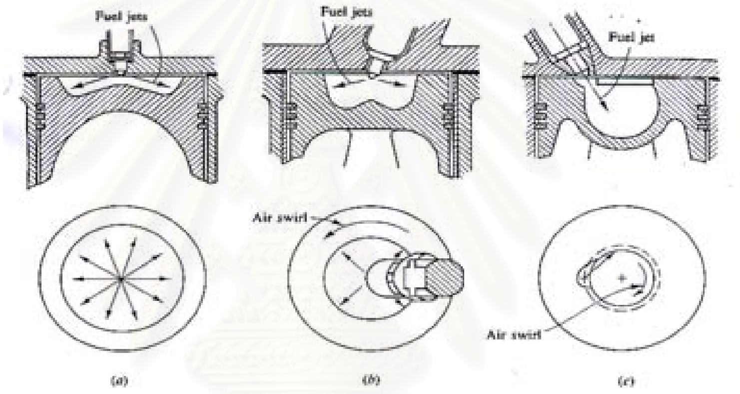


Figure 2.4 Direct injection engine (DI) systems

2.8.2 Indirect-Injection System [10]

Inlet generated air swirl, despite amplification in the piston cup, has not provided sufficiently high fuel – air ratio mixing rates for small high – speed diesels such as those used in automobile. Indirect – injection or divided – chamber engine systems have been used instead, where the vigorous charge motion required during fuel injection is generated during the compression stroke. Two broad classes of IDI systems can be defined:

1) Swirl chamber systems

2) Prechamber systems, as illustrated in Fig. 2.4a and b

During compression, air is forced from the main chamber above the piston into the auxiliary chamber, through the nozzle or orifice. Thus, toward the end of compression, a vigorous flow in the auxiliary chamber is set up; in swirl chamber systems the connecting passage and chamber are shape so that this flow within the auxiliary chamber rotates rapidly.

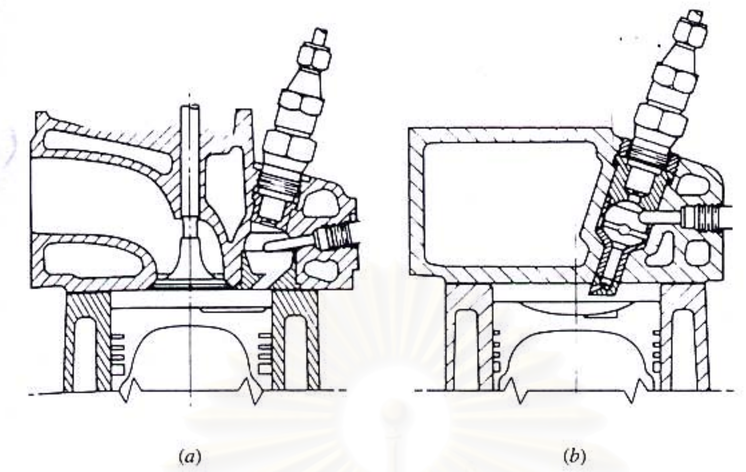


Figure 2.5 Indirect injection engine (IDI) systems

2.9 Thermal Efficiency of Diesel Engine [7]

Thermal efficiencies for gasoline engines are the order of 24%, whereas diesel engines can reach as high as 43% thermal efficiency. The high compression ratio and reduction of air pumping (the decrease of energy required to aspirate the air) along with thermodynamic considerations such as average specific heat of gases present in the cylinder generally explain the higher efficiency of the diesel engine.

In general, the IDI engine has a lower thermal efficiency than DI engine. It has been reported that the DI engine has up to 20% batter fuel efficiency than the IDI engine. The reasons for the lower thermal efficiency of IDI engine (compared to DI engine) include

1) the higher ratio of surface area to volume of combustion chamber (in the cylinder head) and thus a larger loss of heat;
2) thermodynamic losses due to the late combustion process that occurs as the rich pre – chamber mixture expands into the main chamber;
3) the higher friction losses in the small engine operating at higher compression ratios and with heavy mechanical loading.

However the thermal efficiency if IDI engines is small better than of a SI (gasoline) engine.

In the last few decades, Europe and Japan have seen a significant growth in the number of passenger cars fitted with diesel engines, most of which have indirect injection systems. For example, among all the new cars registered in France, diesel – powered cars increased from less than 8% in 1980 to over 28% in 1990; in the UK diesel cars accounted for well over 12% of all registrations in 1992, and the increase in demand for diesel fuel for cars was about 22% in comparison to 7% for gasoline. In Japan, diesel cars accounted for over 20% of all registrations today. For passenger cars in the U.S., the gasoline engine is still supreme, with less than 1% of the market taken by diesel cars in 1998. This is due larger to the fact that low – price gasoline reduces the incentive to adopt the more economical diesel engine for road transportation of passenger (in addition to the environmental regulations on exhaust emissions) in the U.S.

2.10 Exhaust emission sampling system [1]

Diesel engines fitted to passenger cars have to be tested installed in each vehicle to which they are fitted. The vehicle is driven on a chassis dynamometer according to a prescribed drive cycle which simulates urban driving condition (next section). In this case the gaseous emissions, carbon monoxide, carbon dioxide hydrocarbons and the nitrogen oxides are determined using a device called a constant volume sample as shown in Figure 2.6.

The main pump draws air through the dilution tunnel at the constant rate. Into the air stream is introduced the whole of the exhaust gas from the vehicle, the diluting air making up the different between the exhaust flow and the pump flow. A sample of diluted gas, typically of the order of 1% is removed from the gas stream and passed into sample bags. At the end of the prescribed driving distance the content of the bag are analyzed using the relevant analyzers.

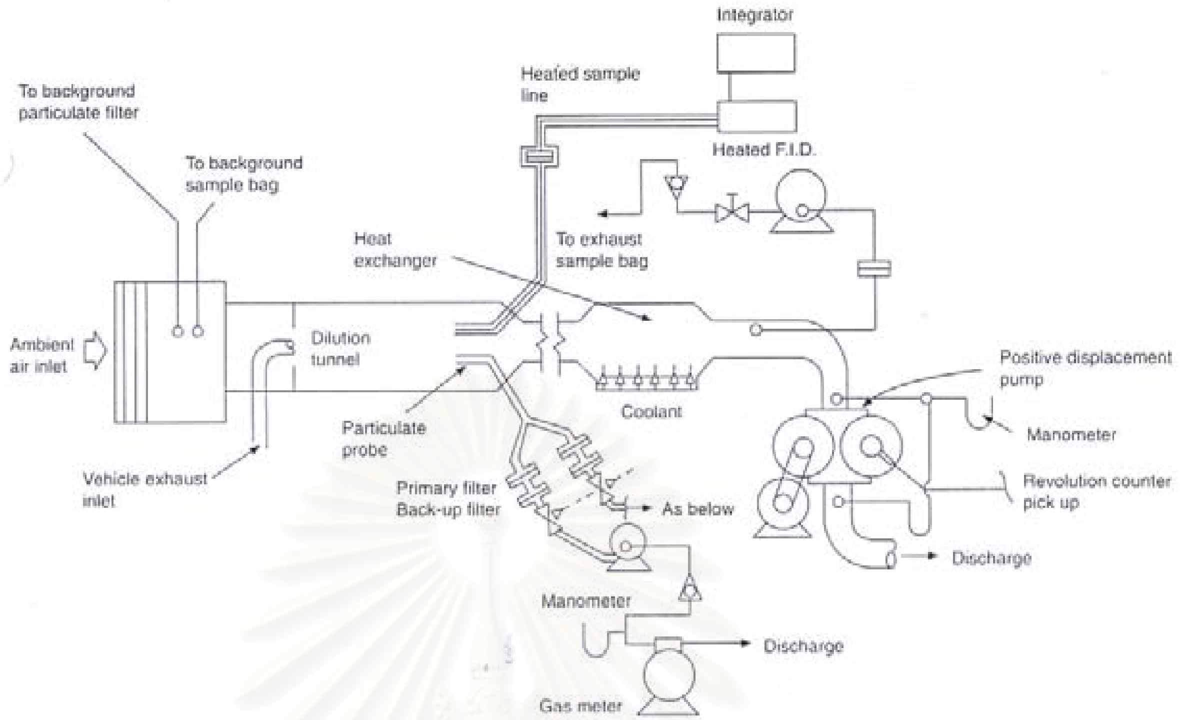


Figure 2.6 Schematic of constant volume sampling for measuring gaseous and particulates emissions.

The hydrocarbons found in diesel exhaust have relatively high boiling point and would, if collected in bags, tend to condense out on the walls giving a spuriously low emission rate. To avoid this, a heated probe continuously removes a sample directly from the dilution tunnel. The sample line to the analyzer are maintained at about 191 °C. It is operated continuously and the readings integrated over the cycle.

Particulate emissions are measured at the same time using the same equipment. A second probe is positioned in the dilution tunnel. To this probe attached a filter, which is of fluorocarbon coated glass fiber, through which a sample is drawn to collect the filterable particulate matter. This filter is subsequently weighed to determine the mass of particulate collected.

2.11 Measurement of exhaust emissions

Exhaust gas emissions need to be measured because of legislation, and also because of the insights the measurement provide into engine performance. The emissions governed by legislation are carbon monoxide (measured by chemiluminescence), unburnt hydrocarbons (measured by flame ionization detector) and particulates. If carbon dioxide (measured by infra-red absorption) and oxygen (measure by a chemical cell, or more accurately by paramagnetism) are also analysed, then it is possible to calculate the air/fuel ratio. Each of these measurement techniques will be described in the following section

2.11.1 Calibration of equipment [1]

With any emissions measuring equipment it is important to test the calibration against (bottled) mixtures of accurately know composition. As a minimum the zero reading and full-scale reading need to be checked. An economical method for checking the linearity of a gas analyzer. the second calibration mixture can of course be air or whatever is being used for the zero checking. The flow meters have to be very accurate over wide range of flows, so the positive displacement domestic gas meters are a good choice. If a second analyzer is available (preferably of a completely different type), the gas flow meters can be dispensed with, at the expense of some compromise in the certainty of the results. If both analyzers indicate a linear response then it is reasonable to assume that they are both indeed linear, since they are unlikely to be non-linear in the same way. This sort of approach is more likely to be acceptable in an academic than an industrial environmental.

2.11.2 Hydrocarbon analysis [2]

The overall hydrocarbon content in diesel-engine exhaust gas is determined using a flame ionization detector analyzer (FID). The FID measuring principle is based on the generation of ions when hydrocarbons are burnt in a hydrogen flame (Fig 2.7). The flow of ions between 2 electrodes is proportional to the atomic C-fraction of the hydrocarbon compound in question.

Display, 2 Burner, 3 Outlet, 4 Hydrogen, 5 Air without HC, 6 Calibrating gas, 7 Exhaust gas.

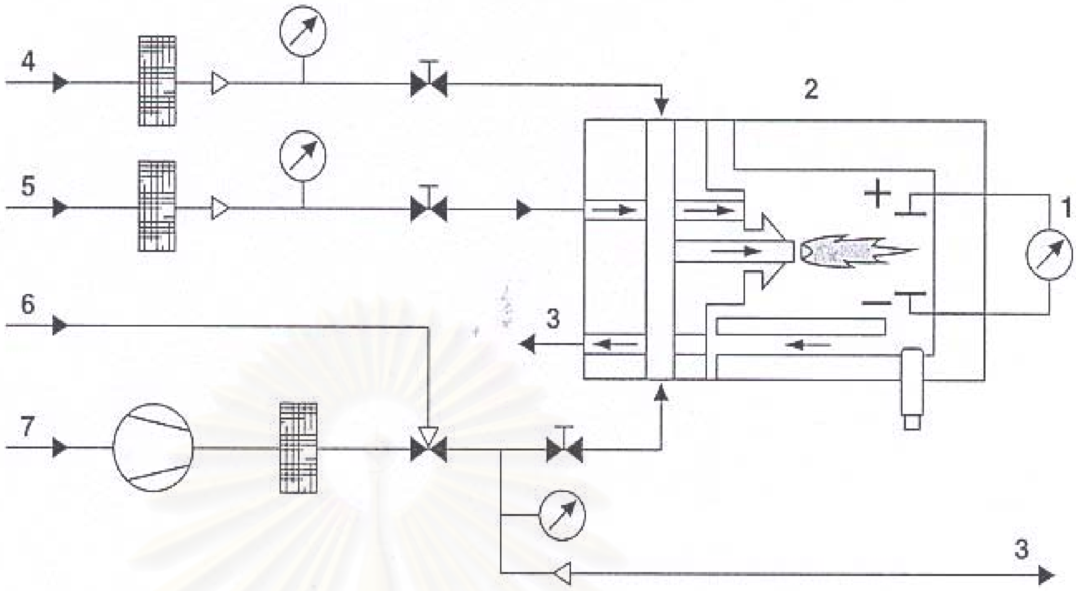


Figure 2.7 FID measurement method for THC analysis

The exhaust gas contains a large number of different hydrocarbon compounds from the engine (consisting individually of unburnt, split, and partially oxidized compounds) which occur in different ratios depending upon the type of fuel and the engine operating mode. The preparation of the test-gas samples is of decisive importance, particularly for hydrocarbon analysis of diesel exhaust emissions. The considerable differences in the condensation temperatures of the individual exhaust-gas components mean that in contrast to the gasoline engine, the diesel test-gas system must be heated continually from the point where the test-gas is extracted right up to entry into the FID burner. The wall temperature of the sampling line system must be maintained at 190° ±10°C.

2.11.3 Carbon-monoxide and Carbon-dioxide analysis [2]

The non-dispersive infrared (NDIR) analyzer process is applied for determining the concentration of these two gaseous components shown in Figure 2.8. This exploits the fact all polyatomic, non-elementary gases absorb infrared radiation in distinct bands specific to each gas. The sample gas is directed through a measuring cell located in the measuring-beam path. A reference cell located in the second beam path is charged with a gas which does not absorb radiation in the wavelengths concerned. A chopper wheel diverts the infrared radiation alternately through one cell and then through the other, so that the radiation finally enters one of the two receiving chambers. These are filled with the gas components which are to be analyzed, and separated from each other by a metal diaphragm in the form of a condenser plate.

1 DC power supply, 2 Amplifier, 3 Mains stabilization, 4 Receiving chamber, 5 Metallic diaphragm, 6 Beam trimmer, 7 Exhaust gas, 8 Measuring cell, 9 Reference cell, 10 Filter cells, 11 Motor-driven chopper, 12 Light source.

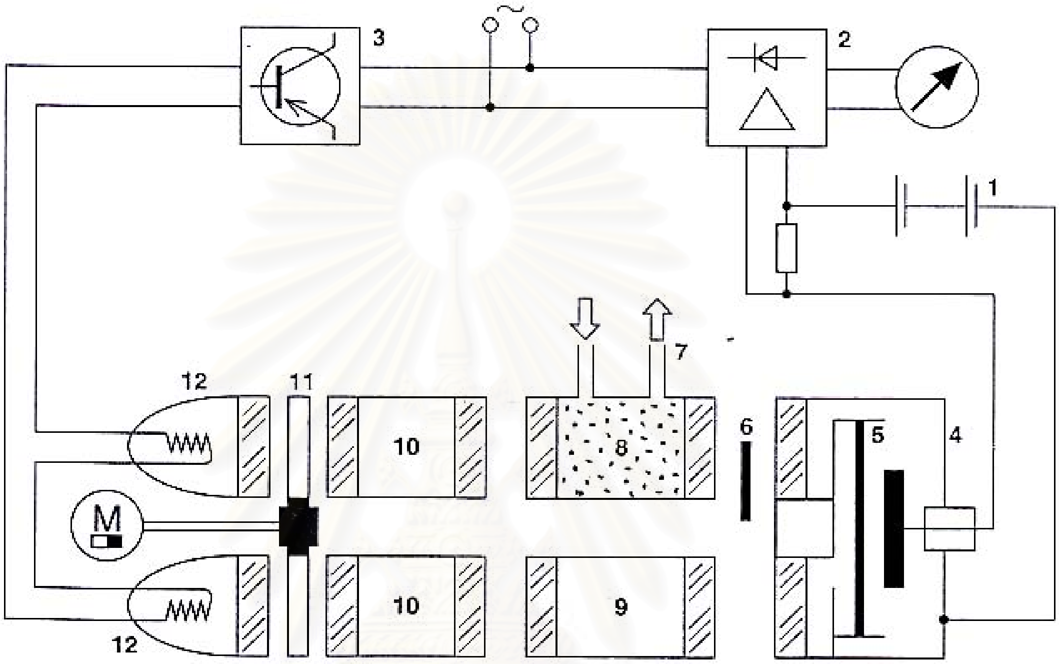
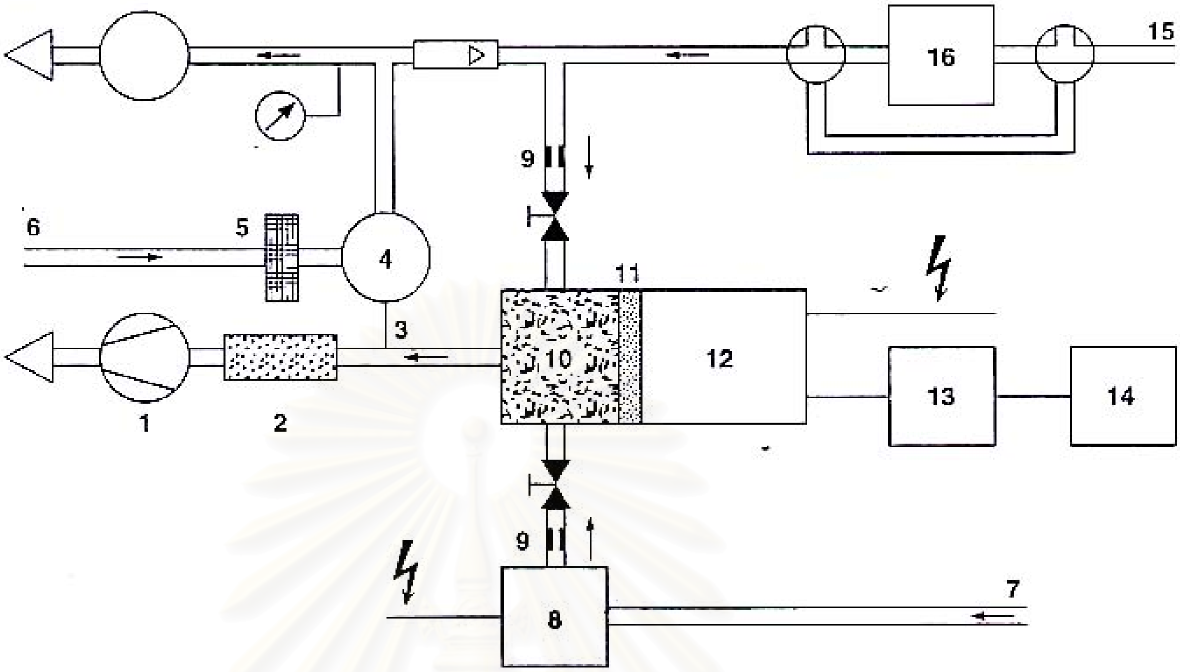


Figure 2.8 NDIR measurement method for CO/CO_2 analysis

The radiation entering the chambers is absorbed only in the specific absorption bands of the gas in the respective chamber, that is, selectively. A difference in the amount of absorbed energy leads to a difference in temperature and pressure between the two chambers. This is converted into a voltage which is proportional to the concentration of the measured components.

2.11.4 Nitrogen-oxide analysis [2]

This measuring principle makes use of chemiluminiscence (chemically generated optical phenomenon) which occurs in the band between 590 and 3,000 nm after reaction of nitrogen oxide (NO) with ozone (O_3) (Figure 2.9).



1 High-vacuum pump, 2 Molecular sieve, 3 Reference line, 4 Quantity regulator, 5 Filter, 6 Air, 7 Oxygen, 8 O_3 generator, 9 Capillary tube, 10 Reaction chamber, 11 Optical filter, 12 Photo-electric multiplier, 13 Amplifier, 14 Indicator device, 15 Exhaust gas, 16 NO_X/NO converter.

Figure 2.9 CLD chemiluminescence detector for NO_X analysis

The gas sample not only contains the nitrogen oxide formed by combustion in the engine, but also products arising from the partial oxidation of NO with the residual oxygen in the exhaust gas. For instance, such nitrogen oxides as NO_2, N_2O, and N_2O_4 are generated in the process. In addition, to NO as the major component, NO_2 can also reach a significant concentration whereas the other nitrogen-oxide compounds lie only slightly above the basic values of the surrounding air. If the total of all nitrogen-oxide compounds (NO_X) in the test gas is to be ascertained, these must be reduced in the “converter” to NO, whereby either thermal or thermo-catalytic methods are used (this process has no effect upon the NO component already present in the test gas). This means that the CLD reaction chamber is only filled with a concentration of pure NO which represents the various nitrogen oxides which have been reduced in the “converter”

The chemiluminescence generated by the introduction of O_3 in the reaction chamber thus corresponds to the overall nitrogen oxide content. In order to eliminate disturbing chemiluminescence caused by other molecules contained in the gas mixture, only the radiation band between 600 and 660 nm is taken into account by using an optical filter.

This selection process and a very low verification limit, the chemiluminescence measuring principle (CLD) is suitable for NO measurement in diluted or undiluted diesel-engine exhaust-gas. Since NO_2 dissolves in water, the test line must be heated to approx. 150±50 °C in order to prevent the condensation of water vapor.

2.11.5 Particulate-matter measurement [2]

Particulates are defined as those exhaust gas components which at a test-gas temperature of 52°C are precipitated on standardized fluoride-carbon-coated glass fiber filters. Mass measurement takes place using differential weighting methods (empty and loaded filters) at constant levels of dampness and temperature. A precision weighing instrument is used. The above definition was drawn up for the first time in US legislation. In the meantime, this test method has become the only generally accepted method in all countries which specify a particulate-emission limit.

2.12 Literature reviews

In 1997, Choi C.Y. *et. al.* [6] studies on the effect on methyl soyate (biodiesel) blends with #2 diesel fuel with various high pressure injection schemes were conducted on a single cylinder version of the Caterpillar 3400 series heavy duty engine. Engine operating conditions at both high and low loads were investigated. Phillips 66 certified #2 diesel fuel was used as the base line; mixtures of 20% and 40% by volume of methyl soyate with the baseline fuel were used as the biodiesel blends. A blend of 20% by volume octadecene (a hydrocarbon’s composition but without the oxygen) in #2 diesel fuel was also investigated to help determine the mechanism of emission reduction.

Under high load condition, a large reduction in particulates with a slight increase in NO_X was observed with the biodiesel blends; the largest particulate reduction was observed with the 40% biodiesel blend case. The 20% biodiesel reduced particulate emissions and additional 36% versus the 20% octadecene blend. With a split injection strategy, the particulates were further reduced for all fuel cases and a decrease in NO_X emissions was observed.

At low load, the addition of biodiesel in the fuel increased the particulate and, overall, NO_X decrease with multiple injections for the low load case. At both high and low engine loads, the percentage of soluble organic fraction (SOF) in the particulate matter increased when biodiesel was blended with diesel #2 diesel fuel.

In 1999, Schröder *et. al.* [19] studied the environmental and health effect deriving from the used of RME in combustion engines. In the 13 – mode test RME leads to higher particle numbers than diesel fuel. The maximum of particle size are similar. In the 5 – mode test, it was found that particulate matter from RME obtains a significantly reduced mutagenic potency compared to diesel fuel.

It was found that the use of RME leads to an increase of ozone precursors in a range of 10 to 30 % compare to fossil diesel fuel. The emissions of aldehydes and alkanes are mainly responsible for this effect. RME leads to both negative and positive effect that cannot be avoided or promoted by blends. There are seem to be a slight disadvantage due to ozone formation. On the other hand, a significant soot reduction and a lower mutagenic potency of the particulate matter is obvious.

In 1999, Choi C.Y. *et. al.* [5] studied on effects of oxygenated fuels in conjunction with single and split fuel injections were conducted at high and low loads on a Caterpillar SCOTE DI diesel engine. At high load, significant beneficial effect of oxygenated fuels was seen to reduce soot emission with little or no penalty on NO_X emissions. Also, at high loads, split injection had an additional favorable effect on soot emissions as compare to single injections, but the soot reducing influence of the oxygenates was not as that seen with the single injection cases. This result indicates that the soot reduction due to the addition of oxygenate to the fuel is most effective in rich combustion as split injection are known to be effective at leaning – out the charge. At low engine loads when the overall mixture is further leaned – out, the oxygenated fuels had only a slight effect on particulate emissions. Split injection were effective in reducing particulate emissions at low loads particularly at advanced fuel injection timing when overall temperature would be expected to be higher.

In 2000, Chistopher A. *et. al.* [4] was investigated the effect of biodiesel fuels on transient emissions from modern diesel engines. Biodiesel was associated with lower engine – out emissions of HC, CO, and particulates compared to levels associated with diesel fuel. These lower emission levels were likely due primary to the fact that biodiesel contains about ten percent oxygen by weight, and this oxygen helps to oxidized these combustion products in the cylinder. HC emissions were generally eliminated, while CO was reduced roughly 40 percent from levels found on diesel. Particulates emissions were reduced between 25 and 50 percent, depending on the engine.

Using biodiesel generally tended to increased NO_X emissions. Substituting neat biodiesel for diesel fuel, NO_X emissions increased by roughly 12 percent, although the Cummins B5.9 engine demonstrated almost no change in NO_X emissions. The oxygen in biodiesel may be the cause of the observed NO_X increased, but this does not explain the lack of NO_X increased in the Cummins B5.9 engine.

Neat biodiesel was generally associated with a loss in engine power of about eight percent for the neat fuel, while B20 power levels were within two percent of observed on diesel fuel. Transient cycle fuel consumption was roughly 13 percent worse with the neat fuel, with B20, transient cycle fuel consumption was essentially the same as with 2D, except for the Cummins B5.9 engine, which showed a six percent increased with B20.

In 2000, Chistopher A. *et. al.* [3] was investigated the effect of biodiesel fuels on transient emissions from modern diesel engines, Unregulated emissions and chemical characterization. It was found that neat biodiesel reduced emissions of aldehydes and ketones substantially. The B20 blend resulted in smaller reductions in aldehydes, although the level of reduction observedwith B20 was much more dependent on the test engine, and varied from none to as much as 30 percent. Neat biodiesel caused large reductions in PAH and NPHA emission, and virtually eliminated some of the heavier NPHA compounds in smaller in reductions in PHA which varied form engine-to-engine, or were not significant for some compounds on some engines. Neat diodiesel caused a dramatic change in the character of the heavier HC species as compared to diesel fuel, with only the esters that made up the biodiesel remaining in exhaust among the higher molecular weight hydrocarbons. B20 heavy HC species represented a mix of diesel and biodiesel compound, although at lower levels than those seen in diesel exhaust (except for the ester which are not present in diesel exhaust). In addition, the blending of biodiesel and diesel did not generate any new species not already present in diesel or biodiesel exhaust.

In 2001, Hamasaki K. *et. al.* [9] utilized the wasted vegetable oil as a diesel fuel, combustion characteristics of waste vegetable oil methyl ester (WME) are examined. Moreover, emulsified waste rapeseed oil methyl ester (EME) is tested the following conclusions are drawn:

1. Result of engines test runs show that the emissions from WME are acceptable; especially smoke emission is lower gas oil.
2. Comparing the combustion state of WME with that of gas oil in the visual engine, WME shows the less soot formation at the point of spray impingement on the piston gas oil.
3. Appling EME with 15% water to engine test run result in not only 18% less NO_X emission accompanied by lower smoke emission but also a few percent less brake specific fuel consumption than WME
4. Burning EME with 15% water in the visual engine, further reduction of soot formation and faster combustion after the end of injection than WME and gas oil be observed.

In 2001, Michael J. *et. al.* [15] studied engine performance of biodiesel fuel prepared from soybean soapstock, the emission data for both the neat fuel and a 20 vol% blend in low – sulfur petroleum diesel were collected according to the Environmental Protection Agency heavy – duty transient cycle protocol using a DDC Series 60 engine on an engine test stand. The emissions profile of biodiesel from soapstock was quite similar to that of biodiesel produced from refined soy oil. Compared with petroleum diesel fuel, emission of total hydrocarbons, particulates, and carbon monoxide were reduced 55%, 53%, and 48%, respectively, with neat soapstock biodiesel. Total nitrogen oxides increased 9%. Operation on a 20 vol% blend of soapstock biodiesel in petroleum diesel gave reductions of 27.7%, 19.7%, and 2.4%, respectively, total hydrocarbon, particulate matter, and carbon monoxide, relative to petroleum diesel. Nitrogen oxide emissions increased 1.3%.

In 2003, McGill R. *et. al.* [14] emission performance of selected biodiesel fuels was investigated, the biodiesel fuels, whether as blends or as neat fuels, increased NO_X emissions but reduced PM emissions. This was true generally at ORNL as well as VTT and with the four different engines that were the subject of experiments reported here. Unregulated emissions of interest – aldehydes and 1,3 –

butadiene – did not seem to have much dependence on the fuel. There were few significant difference in these emissions between the fuels and fuel blends. This was true at both sites. The presence of an oxidation catalyst in the exhaust stream was very effective in the reducing the levels of aldehyde emissions. The oxidation catalysts and the CRT catalyst both had the additional effect of reducing PM emissions, generally with all fuels. With the bus engine, a slight reduction in PAH emissions was observed for the bus engine without catalyst when 30% ester blends were compared with the EN590 fuel. The reduction was significant for neat esters. However, 30% RME blends did not give benefit regarding PAH emissions when compared to the RFD fuel. In the test with after treatment devices the PAH emissions level was so low that no effect of fuel was seen. With the TDI car there was a significant variation of PAH emissions from test to test but it seemed not to be fuel related.

With the bus engine, the neat esters reduced the mutagenicity (Ames test) of particulate SOF comparedto the EN590 fuel in the test without catalyst. The effect of the 30% ester blends was not significant. The oxidation catalyst significantly reduced mutagenicity of particulate SOF, except for RFD and RFD/RME30 fuels, which had low levels regardless of the aftertreatment applied. Even though the mutagenicity level with oxidation catalyst was low, there were some indications that the neat RME give slightly better result than the EN590 fuel.

In 2003, Karhl J. *et. al.* [11] exhaust gas emissions from a modern diesel engine were measured using (1) conventional diesel fuel according to DIN EN 590, (2) Swedish low sulfur diesel fuel MK1, (3) biodiesel, consisting of rape seed oil methyl ester, and (4) a new diesel with lowered boiling characteristics, low sulfur content, and a high level of aromatic compounds. The result showed that:

1. With all fuels, CO emissions are clearly far below the legal limit of 4.0 g/kWh (Uuro II). RME leads to a considerable decrease of CO emissions.
2. For HC emission rates are far below the legal limit of 1.1 g/kWh. RME shows a significant decrease.
3. The NO_X emissions rates lie below the legal limit 7 g/kWh; however, they come quite close to it. This demonstrates that NO_X and, as shown below, PM are the critical components for diesel engines.

4. Particle size distribution; diesel engines are the source of a big part of the emissions of fine particles (diameter less than 2.5 um) and are main source of ultra – fine particles (diameter less than 0.1 um). The four fuels cause quite different emissions. RME leads to more particle in the range of 10 to 40 nm compare to DF and less particle for the larger diameters
5. Aromatic hydrocarbons are mainly found in idle and the modes with light load. In the other modes, the concentration in the exhaust gas is less than 1 ppb, such that they cannot be distinguished from the background concentration. RME leads to a significant reduction of the emissions. As stated already in the introduction, they very different combustion conditions are regarded as being the reason for this discrepancy.
6. Alkenes; concerning the unsaturated hydrocarbons, ethene, ethine, and propene are the main exhaust gas components. As found for the aromatics, they are hardly detectable with exceptions in idle and mode with light load.
7. Aldehydes and ketones contribute to summer smog formation. Aldehydes have a share of 30% to 50% in the overall HC emissions. The results show a reduction of 30% for RME and DF05 comparred to DF, and a slight increase for MK1.

In 2003, Makareviciene V. and Janulis P. [13] were conducted exhaust emission tests on rapeseed oil methyl ester (RME), rapeseed oil ethyl ester (REE) and fossil diesel fuel as well as on their mixtures. The result showed that when considering emissions of nitrogen oxides (NO_X), carbon monoxide (CO) and smoke density, rapeseed oil ethyl ester had less negative effect on the environmental in comparison with that of rapeseed oil methyl ester. When fuelled with rapeseed oil ethyl ester, the emission of NO_X showed an increase of 8.3% over those of fossil diesel fuel. When operate on 25 – 50% biodiesel mixed with fossil diesel fuel, NO_X emissions marginally decreased. When fueled with pure rapeseed oil ethyl ester, HC emissions decreased by 53%, CO emissions by 7.2% and smoke density 72.6% when compare with emissions when fossil diesel fuel was used. Carbon dioxide (CO_2)

emissions decreased by 782.87 g/kWh when rapeseed oil ethyl ester was used and by 782.26 g/kWh when rapeseed oil methyl ester was used instead of fossil diesel fuel.

In 2003, Dorado M.P. *et. al.* [8] studied the exhaust emissions of diesel direct injection Perkins engine fueled with waste olive oil methyl ester. Emission were characterized with neat biodiesel from used olive oil and conventional diesel. Result revealed that the use of biodiesel resulted in lower emission of CO (up to 58.9%), CO_2 (up to 8.6%, expecting a case which present a 7.4% increase), NO (up to 37.5%), and SO_2 (up to 57.7%), with increase in emission of NO_2 (up to 81%, expecting a case which presented a slight reduction). Biodiesel also presented a slight increase in brake – specific fuel consumption (lower than 8.5%).

In 2004, Nwafor O.M.I. [16] was evaluated the potential of rapeseed methyl ester (RME) as a liquid fuel for diesel engines in relation to meeting emission requirements. The test results showed that RME and its blends with diesel fuel emitted high CO_2 compared to test results on diesel fuels. A very significant reduction in emissions of hydrocarbon (HC) were recorded when running or RME and the blends. HC emissions were noted to increase with increased amount of diesel fuel in blend. The fuel economy was a little worse when running on RM and the blends. HC emissions were noted to increased with increase amount of diesel fuel in the blend. The fuel economy was a little worse when running on RME due to its low energy content.

In 2004, Win lee S. et. al. [22] was examined combustion performance of a blend containing 20% soybean methyl ester in heating No.2 using a residential – scale hot water boiler. The blend burned satisfactory with no modifications to the appliance and fuel delivery system. SO_2 emissions were 19.7 ± 2.5% lower than that of No. 2 fuel while NO_X emissions were similar. Particulate emissions, as determined by source dilution measurement system, were on average 15.7 ± 6.15%. Potential reductions of $PM_{2.5}$, SO_2 and green house gas emissions for the petroleum distillates that can be replace with biodiesel.

In 2005, Lapuerta M. *et. al.* [12] methyl ester obtained from the most interesting Spanish oleaginous crops for energy use – sunflower and *Cynara* carduncului – were both used as diesel fuels, pure and in 25% blends with a commercial fuel which was also used pure. A stationary engine test bed, together with the instrumentation for chemical and morphological analysis, allowed to study the effect of these fuels on the engine emissions, soluble organic fraction of the particulate matter, origin of adsorbed hydrocarbons, sulfhate content, particle number per unit filter surface, and mean particle diameter.

1. Particulate emissions were reduced for every mode tested as the concentration of any of the tested biodiesel fuels were increased in the blend
2. The presence of oxygen on the ester molecules did not lead to increase in NO_X formation. On the contrary a certain decrease was observed at high load.
3. With respect to reference commercial fuels, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased.
4. The proportion of adsorbed hydrocarbons on the particles surface (SOF) increased with the biodiesel concentration.
5. The major contribution to SOF came from lube oil for all the tested modes and fuels, and this proportion became even higher as the biodiesel concentration was increased.
6. The sulphate content in the particulate matter was also reduced, consistently with the sulphur reduction in the fuel. Highest reductions were found with sunflower methyl ester.
7. The presence of vegetable esters in the fuel led to dramatic decreases in the number of particles.

CHAPTER III

EXPERIMENTAL

3.1 Instrument and apparatus

3.1.1 Instrument and apparatus for exhaust emissions testing

The exhaust emissions analysis were carried out by using chassis dynamometer which connected with analyzer of AVL analyzer for analysis CO,CO_2, NO_X, THC, PM emissions.

CVS test method for passenger cars and light commercial vehicles

1 Blower, 2 Dynamometer, 3 Air, 4 Filter, 5 Pump, 6 Dilution tunnel, 7 Flow meter, 8 Gas counter, 9 Heat exchanger/heater, 10 Burner, 11 Airbag, 12 Calibrating gas, 13 Zero gas, 14 Exhaust-gas sample bag, 15 Heated line, 16 Roots-blower, 17 Extraction, 18 Integrator, 19 Computer, 20 Recorder.

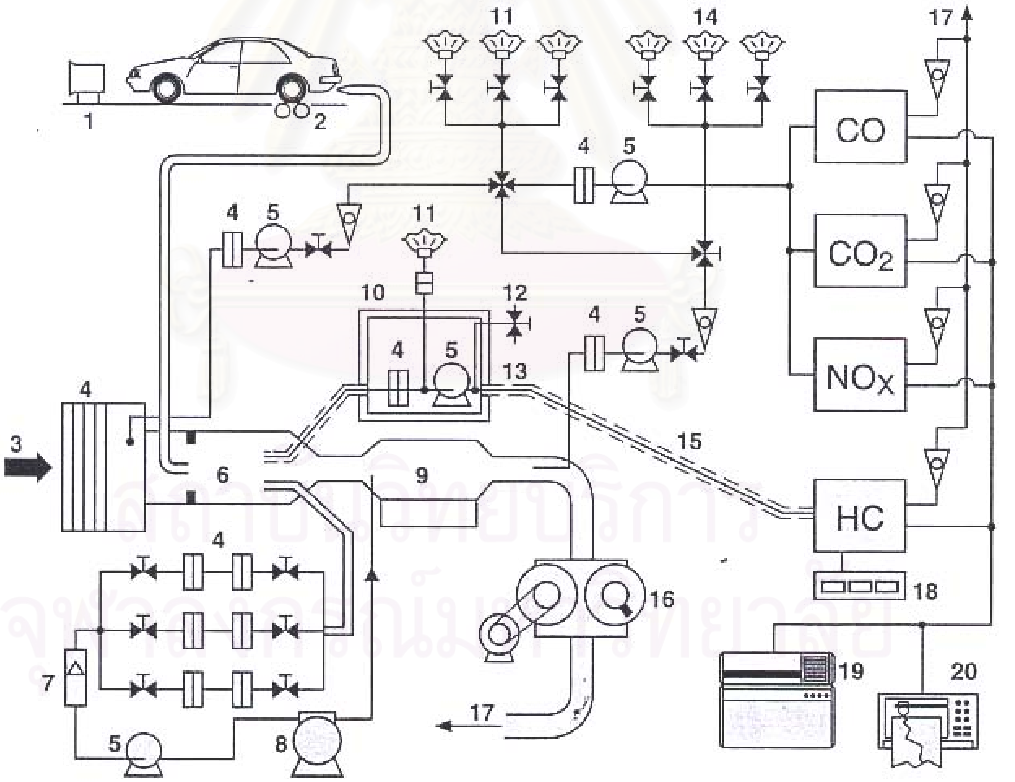


Figure 3-1 Chassis dynamometer and CVS test method for passenger cars and light commercial vehicle

3.1.2 Instrument and apparatus for testing physical and chemical properties of biodiesel, biodiesel blended fuels and diesel fuels.

1. Flash point tester
2. Centrifuge
3. Kinematics Viscometer
4. Carbon residue tester
5. Furnace
6. Sulfur analyzer
7. Copper strip corrosion tester
8. Cloud point tester
9. TAN &TBN tester
10. CFR Engine
11. Gas Chromatograph
12. Distillation tester
13. Density meter
14. Gross heat of combustion tester
15. Elemental analyzer
16. ICP
17. Hydrometer
18. HFRR
19. Colour tester

3.2 Chemicals and Materials

3.2.1. Used cooking oil was bought from frying food shops.

3.2.2. NaOH commercial grade

3.2.3. Methanol commercial grade

3.2.4 Standard Reference gas from Thai industrial gas (TIG)

3.2.5 Acetic acid from Lab Scan

3.2.6 Palm strearin methyl ester

3.2.7 Rapeseed methyl ester

3.3 Test Cars

Test cars are 2 diesel engines. The specification of the test cars and Road Load Simulation data were shown in Table 3.1 and Table 3.2.

1. Toyota D4D 2.5L, transmission 5-M/T
2. Isuzu DMAX 2.5L, transmission 5-M/T

Table 3.1 The Specification of Test Cars.

Description	Test car	
	Isuzu DMAX	Toyota D4D
Car Maker	Isuzu Motor Thailand	Toyota Manufacturing Thailand
Vehicle Model	Isuzu DMAX single cab	Hilux Tiger D4D single cab
Model year	2003	2003
Odermeter (km)	77,000	41,000
Engine Type	4JA1	2KD-FTV
Chassis No.	2W120 FTR54HSM1XAS	MR031JNF500007784
Engine No.	BK3380	2KD-9077393
Displacement (cc.)	2499	2494
Transmission	5-M/T	5-M/T
Vehicle weight (kg)	1650	1390
Number of cylinder	4	4
Bore / Stroke	93.0 / 92.0	92.0 / 93.8
Compression ratio	17.7:1	18.5:1
Injection system	DI, Rotary Pump	DI, Commonrial
Cooling system	Water cooled	Water Cooled
Catalytic Converter	OC	OC
Idling speed (rpm)	730	700
Max. Power, ECC net (kW) @rpm	58 / 3900	75 / 3800
Max. Torque, EEC net (N-m)@rpm	215 / 1800	200 / 1400-3200

Table 3.2 Road Load Simulation data

Description	**Isuzu DMAX**	**Toyota D4D**
Road load equation (N)	$F=0.04418*V^2 - 1.00442*V + 173.71313$	$F=0.05652*V^2 - 0.97267*V +155.33783$
Inertia weight	1810	1470
Vehicle weight	1650	1390
Reference mass	1750	1490

3.4 Test Fuels

The base diesel fuels used in this study were purchased from the PTT public company limited. Thailand Biodiesel, B100T, (Palm Stearin Methyl Ester, PSME), according to ASTM D6751, obtained from Thailand Institute of Science and Technological Research (TISTR). Germany Biodiesel, B100F, (Rapeseed Methyl Ester, RME) according to EN 14214, obtained from BIO-Diesel Wittenberge GmbH, Wittenberge, Germany. Biodiesel from Used cooking oil (UCME) were prepared according to the condition as described below:

1. Base diesel : BDS
2. BDS + 2% PSME : B2T
3. BDS + 2% RME : B2F
4. BDS + 5% PSME : B5T
5. BDS + 5% RME : B5F
6. BDS + 20% PSME : B20T
7. BDS + 20% RME : B20F
8. BDS + 20% UCME : B20U
9. BDS + 30% UCME : B30U
10. BDS + 40% UCME : B40U
11. 100% PSME : B100T
12. 100% RME : B100F

Preparation of Biodiesel from used cooking oil

The transesterifacation of used cooking oil was carried out in the 10 liters stainless container, the condition is shown below:

Temperature 50 °C	
Ratio of oil per methanol	4.5 : 1 liter
Amount of NaOH per liter of oil	8 – 10 gram
Reaction time	1 hour.

Then methyl ester was separated and cleaned with water. The water was evaporated at 70 °C for 3 hours, finally the pure methyl ester was obtained.

3.5 Exhaust emissions analysis

Diesel engines were tested on Chassis Dynamometer. Exhaust emission analysis following to TIS 2155 – 2546 which equivalent to European emissions analysis standard method (Directive 1999/102/EC, EURO 3 test cycle).

The regulated emissions (THC, CO, CO_2, NO_X, Particulate matter) were taken to Tedlar bag by using CVS (Constant Volume Sampling) which can be seen from step 6 in Figure 3.1. After the end of test cycle, the exhaust emissions were determined.

1. Total hydrocarbons (THC) is analyzed using a flame ionization detector (FID).
2. Carbon dioxide (CO_2) and carbon monoxide (CO) are analyzed using non – dispersive infrared detector (NDIR).
3. Nitrogen – oxide (NO_X) is analyzed using chemiluminescence detector (CLD).
4. Particulate matter (PM) is analyzed d by drawing exhaust emissions through a filter (70 mm diameter Teflon coated glass fiber (T60A20,Pall/Gelman) maintained at 52 °C, and computing the change in filter weight. The fuel consumption is calculated by Carbon balance method.

3.6 Exhaust Emission Test Procedure [2]

Light duty vehicles are generally taken as those not exceeding 3500kg gross vehicle weigh. The test procedure is now that specified in the ECE Regulation 15, with the addition of the Extra Urban Driving Cycle (EUDC). In the basic cycle the vehicle is driven four times without interruption over the prescribed 15 modes to give a total distance of 4 km. A constant volume sampling system is used, Carbon monoxide, carbon dioxide. Hydrocarbons and nitrogen oxides are measured and also emissions of particulate matter (PM).

The ECE+EUDC test cycle is performed on a chassis dynamometer. The cycle used for emission certification of light duty vehicles in Europe. The entire cycle includes four ECE segments, Figure 3-2, repeated without interruption, followed by one EUDC segment, Figure 3-3. Before the test, the vehicle is allowed to soak for at least 6 hours at a test temperature of 20-30°C. It is then started and allowed to idle for 40s.

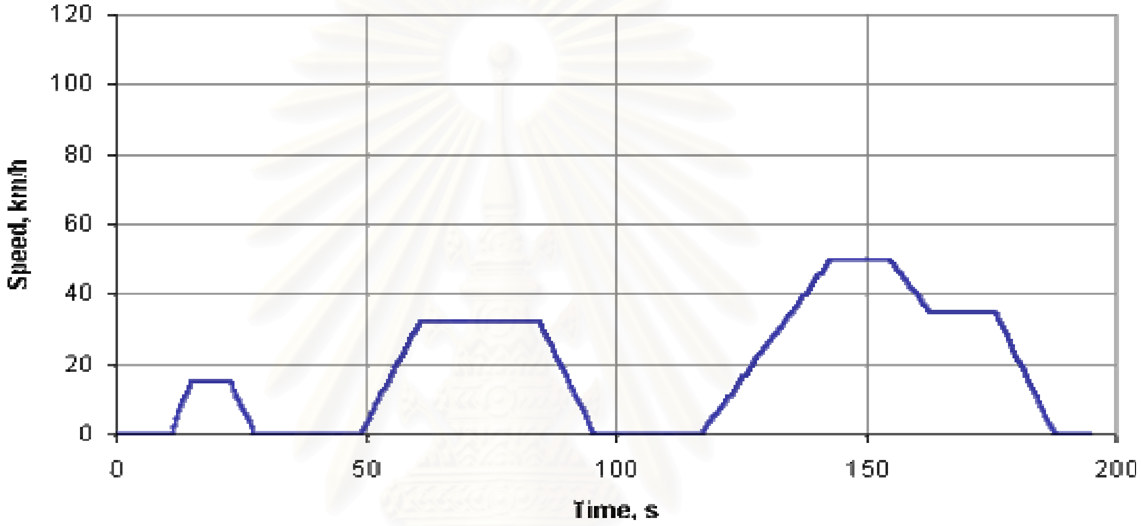


Figure 3.2 ECE test cycle

Effective year 2000, that idling period has been eliminated, i.e., engine starts at 0s and the emission sampling begins at the same time.

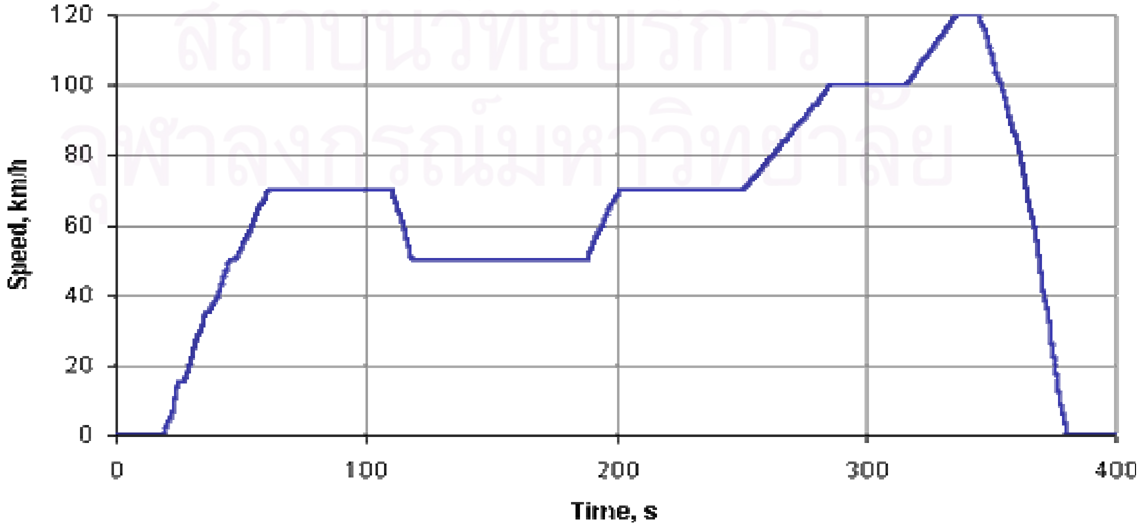


Figure 3.3 EUDC test cycle

Emissions are sampled during the cycle according the “Constant Volume Sampling” technique, analyzed, and expressed in g/km for each of the pollutants.

The EUDC (Extra Urban Driving Cycle) segment has been added after the fourth ECE cycle to account for more aggressive, high speed driving modes. The maximum speed of the EUDC cycle is 120 km/h. The following table includes a summary of the parameters for both the ECE and EUDC cycles.

Table 3.3 Summary of test cycle

Characteristics	**Unit**	**ECE 15**	**EUDC**
Distance	km	4*1.013 = 4.052	6.955
Duration	s	4*195=780	400
Average speed	km/h	18.7(with idling)	62.6
Maximum speed	km/h	50	120

3.7 Data Grouping for Analysis

The tests data were grouping before statistical analysis in order to corrected the tests data caused by time dependence. The group of data as shown in Table 3.4

Table 3.4 Data grouping for T-test analysis

Test Items	**Group No.**	**Test Fuels**	**Baseline**
Regulated emissions and fuel consumption	1	B2T, B5T	BDS Avg 1
	2	B20T, B100T	BDS Avg 2
	3	B2F, B5F	BDS Avg 3
	4	B20F, B100F	BDS Avg 4
	5	B20U,B30U, B40U	BDS Avg 5

CHAPTER IV

RESULTS AND DISCUSSION

This chapter described the testing results of research, which composes of three parts. The first part shows chemical and physical properties of three kinds of methyl ester (used cooking oil methyl ester, palm strearin methyl ester, rapeseed methyl ester) according to ASTM D6751 specification. Second part shows the chemical and physical properties of test fuels that are three kinds of methyl ester blended with base diesel, which was tested by Department of business energy standard. The last one is a discussion of the effect of methyl ester and methyl ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L and Isuzu DMAX 2.5L.

4.1 Identification of biodiesel

Used Cooking Oil Methyl Ester was transesterified at temperature 50 °C by using sodium hydroxide as catalyst and mixed for 1 hour. The 70-80% yields of the mixture of methyl esters were obtained. The chemical and physical properties of used cooking oil methyl ester were tested according to ASTM D6751 shown in Table 4.1.

The chemical and physical properties of palm stearin methyl ester (PSME) that obtained from Thailand Institute of Science and Technology Research (TISTR) shown in Table 4.2.

The chemical and physical properties of rapeseed methyl ester (RME) that obtained from BIO-Diesel Wittenberge GmbH, Wittenberge, Germany which shown in Table 4.3.

The flash point value of all methyl ester in Table 4.1, 4.2 and 4.3 indicated that methyl ester has much higher than base diesel fuel. The kinematic viscosity of all methyl ester higher than base diesel, however, it’s not over specification limit according to ASTM D6751. All methyl ester are low sulfur and contain about 10wt% oxygen. Specific gravity of methyl ester has slightly higher than base diesel fuel. Palm stearin methyl ester has highest cetane number, 68.8 whereas used cooking oil methyl ester has cetane number 60.5 and the lowest cetane number is rapeseed methyl ester, 50.3. Gross heating value of all methyl ester is about 12% lower than base diesel fuel. All methyl ester have no corrosion. Therefore, result of copper strip corrosion was No. 1.

Table 4.1 Chemical and physical properties of B100U (Used Cooking Oil Methyl Ester) following by ASTM D 6751 specification.

Fuel Properties	**Test Method**	**ASTM D6751 Specification**	**B100U**
Flash point, ˚C	ASTM D93	130.0 min	158.0
Water and sediment, %vol.	ASTM D2709	0.050 max	trace
Kinematic Viscosity at 40 ˚C, cSt.	ASTM D445	1.9-6.0	4.722
Carbon Residue, %wt.	ASTM D4530	0.050 max	0.062
Sulfate ash, %wt.	ASTM D874	0.020 max	<0.001
Sulfur content, %wt.	ASTM D5453	0.0015 max	0.0013
Copper strip corrosion, No.	ASTM D130	No.3 max	1a
Cloud point, ˚C	ASTM D2500	Report	13.0
Total acid number, mgKOH/g	ASTM D664	0.80 max	0.50
Cetane number	ASTM D613	47 min	60.5
Phosphorus content, ppmwt.	ASTM D4951	0.001 max	n.d.
Free glycerin, %mass	ASTM D6584	0.020	-
Total glycerin, %mass	ASTM D6584	0.240	-
Distillation			
AET at 90%recovered, ˚C	ASTM D1160	360 max	356
Specific gravity @ 15.6/15.6 ˚C	ASTM D1298	-	0.8822
Gross heating value, J/g	ASTM D240	-	39589
Carbon, %mass	Modified ASTMD5291	-	76
Hydrogen, %mass	Modified ASTMD5291	-	13
Oxygen, %mass	Modified ASTMD5291	-	10

Table 4.2 Chemical and physical properties of B100T (Palm Stearin Methyl Ester) following by ASTM D 6751 specification.

Fuel Properties	**Test Method**	**ASTM D6751 Specification**	**B100T**
Flash point, ˚C	ASTM D93	130.0 min	171
Water and sediment, %vol.	ASTM D2709	0.050 max	Trace
Kinematic Viscosity at 40 ˚C, cSt.	ASTM D445	1.9-6.0	4.689
Carbon Residue, %wt.	ASTM D4530	0.050 max	0.031
Sulfate ash, %wt.	ASTM D874	0.020 max	<0.001
Sulfur content, %wt.	ASTM D5453	0.0015 max	0.0002
Copper strip corrosion, No.	ASTM D130	No.3 max	No. 1a
Cloud point, ˚C	ASTM D2500	Report	18
Total acid number, mgKOH/g	ASTM D664	0.80 max	0.19
Cetane number	ASTM D613	47 min	68.8
Phosphorus content, ppmwt.	ASTM D4951	0.001 max	n.d.
Free glycerin, %mass	ASTM D6584	0.020	n.d.
Total glycerin, %mass	ASTM D6584	0.240	0.13
Distillation			
AET at 90%recovered, ˚C	ASTM D1160	360 max	352
Specific gravity @ 15.6/15.6 ˚C	ASTM D1298	-	0.8745
Gross heating value, J/g	ASTM D240	-	40168
Carbon, %mass	ModifiedASTMD5291	-	76
Hydrogen, %mass	ModifiedASTMD5291	-	13
Oxygen, %mass	ModifiedASTMD5291	-	10

Table 4.3 Chemical and physical properties of B100F (Rapeseed Methyl Ester) following by ASTM D 6751 specification.

Fuel Properties	**Test Method**	**ASTM D6751 Specification**	**B100F**
Flash point, ˚C	ASTM D93	130.0 min	182
Water and sediment, %vol.	ASTM D2709	0.050 max	trace
Kinematic Viscosity at 40 ˚C, cSt.	ASTM D445	1.9-6.0	4.491
Carbon Residue, %wt.	ASTM D4530	0.050 max	0.015
Sulfate ash, %wt.	ASTM D874	0.020 max	<0.001
Sulfur content, %wt.	ASTM D5453	0.0015 max	0.0015
Copper strip corrosion, No.	ASTM D130	No.3 max	No.1a
Cloud point, ˚C	ASTM D2500	Report	-5
Total acid number, mgKOH/g	ASTM D664	0.80 max	0.35
Cetane number	ASTM D613	47 min	50.3
Phosphorus content, ppmwt.	ASTM D4951	0.001 max	n.d.
Free glycerin, %mass	ASTM D6584	0.020	-
Total glycerin, %mass	ASTM D6584	0.240	-
Distillation			-
AET at 90%recovered, ˚C	ASTM D1160	360 max	355
Specific gravity @ 15.6/15.6 ˚C	ASTM D1298	-	0.8836
Gross heating value, J/g	ASTM D240	-	40028
Carbon, %mass	ModifiedASTMD5291	-	77
Hydrogen, %mass	ModifiedASTMD5291	-	13
Oxygen, %mass	ModifiedASTMD5291	-	10

4.2 Identification of biodiesel blended with diesel fuels.

Diesel fuel from PTT Public company Ltd. was used as base fuel in this study. Used cooking oil methyl ester was blended with base diesel fuels in ratio 2, 5, 10, 20, 30, 40 and 50 volume percent, palm stearin methyl ester was blended with base diesel fuel in ratio 2, 5 and 20 volume percent, as well as rapeseed methyl ester was blended with base diesel fuel in ratio 2, 5 and 20 volume percent. The chemical and physical properties of these methyl ester blended fuels according to Department of energy business standard specification were shown in Table 4.4, 4.5, 4.6 and 4.7.

As specific gravity of all methyl ester are higher than base diesel, therefore, methyl ester blended with base diesel fuel results in higher specific gravity. When the kinematics viscosity of blended methyl ester with base diesel fuel was slightly increased, but it's not over of specification limit according to Department of energy business standard. Sulfur content in methyl ester blended fuel was decreased as increasing volume percent of methyl ester because methyl ester contained low concentration of sulfur compounds as a result it emits the low SO_2 in exhaust emissions which the primary component of acid rain.

The flash point of methyl ester blended fuels was slightly higher than of base diesel so the methyl ester blended fuels are safer to store, handle and use. The cetane number of methyl ester blended fuels was increased with increasing volume percent of methyl ester blended fuel which due to the increase of the oxygenated compounds in the methyl ester.

Lubricity performance describes how a fuel lubricates the fuel system and engine part especially pumps system. The result of methyl ester blended fuel was shown that the increasing amount of methyl ester blended with base diesel fuel the lubricity performance was increased. The experimental result shows blended palm stearin methyl ester 2 volume percent with base diesel, the lubricity performance increases 2 times. The distillation temperature at 90% recovery of methyl ester blended fuels decrease with increased amount of methyl ester blended due to reduced PM in exhaust emissions of diesel engine.

All methyl ester have 13% less heating value than base diesel. Therefore, heating value of methyl ester blended fuels were decreased with increasing volume percent of methyl ester blended which concerning about fuel consumption the results were shown in Table 4.4, 4.5, 4.6 and 4.7.

Table 4.4 Chemical and physical properties of Used Cooking Oil Methyl Ester blended with diesel fuels (following by Department of Energy Business Standard).

Fuel Properties	Test Method	BDS	B2U	B5U	B10U
Specific gravity at 15.6/15.6 ˚C	ASTM D1298	0.8343	0.8350	0.8363	0.8387
Calculated Cetane Index	ASTM D976	56.2	56.2	56.1	55.9
Cetane Number	ASTM D613	58.6	59.3	58.4	58.4
Viscosity at 40 ˚C (cSt)	ASTM D445	2.879	2.900	2.924	2.994
Pour point (˚C)	ASTM D97	-3	-3	-3	-3
Sulfur Content (%wt.)	ASTM D4294	0.0274	0.0272	0.0261	0.0249
Copper Strip Corrosion (No.)	ASTM D130	1a	1a	1a	1a
Carbon residue (%wt.)	ASTM D4530	0.014	0.001	0.001	0.001
Water and sediment (%vol.)	ASTM D2709	traces	traces	traces	traces
Ash (%wt.)	ASTM D482	0.001	0.001	<0.001	<0.001
Flash point (˚C)	ASTM D93	63.0	64.0	64.0	66.0
Distillation					
90% recovered (˚C)	ASTM D86	354.1	354.4	353.9	352.3
Colour	ASTM D1500	0.5	0.5	L1.0	L1.5
Lubricity Performance (µm)	CFCF06A96	-	-	-	-
Gross Heating Value (J/g)	ASTM D240	45743	45609	45359	45119
Aromatic Content (%)	IP 391/95				
Monoaromatic, g/100ml		-	-	-	-
Diaromatic, g/100ml		-	-	-	-
Polyaromatic, g/100ml		-	-	-	-
Total aromatic, g/100ml		-	-	-	-
Carbon, %mass		84	85	84	82
Hydrogen, %mass		13	14	14	14

Table 4.5 Chemical and physical properties of Used Cooking Oil Methyl Ester blended with diesel fuels (following by Department of Energy Business Standard (cont.).

Fuel Properties	**Test Method**	**B20U**	**B30U**	**B40U**	**B50U**
Specific gravity at 15.6/15.6 ˚C	ASTM D1298	0.8433	0.8481	0.8529	0.8578
Calculated Cetane Index	ASTM D976	55.3	54.6	53.6	52.5
Cetane Number	ASTM D613	59.0	58.4	58.4	59.0
Viscosity at 40 ˚C (cSt)	ASTM D445	3.1321	3.2918	3.4492	3.6495
Pour point (˚C)	ASTM D97	-3	-3	0	0
Sulfur Content (%wt.)	ASTM D4294	0.0223	0.0192	0.0166	0.0142
Copper Strip Corrosion (No.)	ASTM D130	1a	1a	1a	1a
Carbon residue (%wt.)	ASTM D4530	0.001	0.001	0.001	0.001
Water and sediment (%vol.)	ASTM D2709	traces	traces	traces	traces
Ash (%wt.)	ASTM D482	<0.001	<0.001	<0.001	<0.001
Flash point (˚C)	ASTM D93	68.0	71.0	76.0	80.0
Distillation					
90% recovered (˚C)	ASTM D86	351.4	350.6	349.4	348.4
Colour	ASTM D1500	L1.5	L2.0	L2.0	2.5
Lubricity Performance (μm)	CFCF06A-96	-	-	-	-
Gross Heating Value (J/g)	ASTM D240	44408	43854	43225	42562
Aromatic Content (%)	IP 391/95				
Monoaromatic, g/100ml		-	-	-	-
Diaromatic, g/100ml		-	-	-	-
Polyaromatic, g/100ml		-	-	-	-
Total aromatic, g/100ml		-	-	-	-
Carbon, %mass		83	82	81	80
Hydrogen, %mass		13	13	13	13

Table 4.6 Chemical and physical properties of Palm Stearin Methyl Ester blended with diesel fuels (following by Department of Energy Business Standard).

Fuel Properties	Test Method	BDS	B2T	B5T	B20T
Specific gravity at 15.6/15.6 ˚C	ASTM D1298	0.8276	0.8279	0.8295	0.8363
Calculated Cetane Index	ASTM D976	57.6	57.5	57.5	57.2
Cetane Number	ASTM D613	57.4	59.5	57.6	58.5
Viscosity at 40 ˚C (cSt)	ASTM D445	2.698	2.887	2.924	3.132
Pour point (˚C)	ASTM D97	-3.0	-3.0	-3.0	-3.0
Sulfur Content (%wt.)	ASTM D4294	0.030	0.032	0.031	0.023
Copper Strip Corrosion (No.)	ASTM D130	1a	1a	1a	1a
Carbon residue (%wt.)	ASTM D4530	0.001	<0.001	0.001	0.001
Water and sediment (%vol.)	ASTM D2709	traces	traces	traces	traces
Ash (%wt.)	ASTM D482	<0.001	<0.001	<0.001	<0.001
Flash point (˚C)	ASTM D93	61	61.5	62.5	61.5
Distillation					
90% recovered (˚C)	ASTM D86	353.2	350.4	349.2	344.1
Colour	ASTM D1500	L0.5	L1.0	L1.0	L1.0
Lubricity Performance (μm)	CFCF06-A-96	433	181	187	211
Gross Heating Value (J/g)	ASTM D240	45,842	45,897	45,587	44,956
Aromatic Content (%)	IP 391/95				
Monoaromatic, g/100ml		20.6	-	-	-
Diaromatic, g/100ml		4.4	-	-	-
Polyaromatic, g/100ml		0.3	-	-	-
Total aromatic, g/100ml		25.3	-	-	-
Carbon, %mass		86.22	-	-	-
Hydrogen, %mass		13.78	-	-	-

Table 4.7 Chemical and physical properties of Rapeseed Methyl Ester blended with diesel fuels (following by Department of Energy Business standard specification).

Fuel Properties	**Test Method**	**BDS**	**B2F**	**B5F**	**B20F**
Specific gravity at 15.6/15.6 ˚C	ASTMD1298	0.8276	0.8282	0.8297	0.8381
Calculated Cetane Index	ASTM D976	57.6	57.5	57.4	57.0
Cetane Number	ASTM D613	57.4	60.0	57.6	56.1
Viscosity at 40 ˚C (cSt)	ASTM D445	2.698	2.884	2.917	3.101
Pour point (˚C)	ASTM D97	-3.0	-3.0	-3.0	-3.0
Sulfur Content (%wt.)	ASTMD4294	0.030	0.032	0.031	0.023
Copper Strip Corrosion (No.)	ASTM D130	1a	1a	1a	1a
Carbon residue (%wt.)	ASTMD4530	0.001	0.001	<0.001	0.001
Water and sediment (%vol.)	ASTMD2709	traces	traces	traces	traces
Ash (%wt.)	ASTM D482	<0.001	<0.001	<0.001	<0.001
Flash point (˚C)	ASTM D93	61	62.5	60.5	63.5
Distillation					
90% recovered (˚C)	ASTM D86	353.2	349.8	349.1	347.7
Colour	ASTMD1500	L0.5	L1.0	L1.0	L1.0
Lubricity Performance (µm)	CFCF06A-96	433	213	202	210
Gross Heating Value (J/g)	ASTM D240	45,842	45,762	45,548	45,537
Aromatic Content (%)	IP 391/95				
Monoaromatic, g/100ml		20.6	-	-	-
Diaromatic, g/100ml		4.4	-	-	-
Polyaromatic, g/100ml		0.3	-	-	-
Total aromatic, g/100ml		25.3	-	-	-
Carbon, %mass		86.22	-	-	-
Hydrogen, %mass		13.78	-	-	-

4.3 The effect of Used Cooking Oil Methyl Ester blended fuels on Exhaust emissions and fuel consumption of Toyota D4D 2.5 L and Isuzu DMAX 2.5L.

Two light – duty diesel vehicles, Toyota D4D 2.5L and Isuzu DMAX 2.5L were selected for this study. Because their market share are totally nearly 80% in Thailand. The test vehicle were operated on chassis dynamometer which tested with 4 kinds of test fuels: based diesel fuel, 20% used cooking oil methyl ester (B20U), 30% used cooking oil methyl ester (B30U) and 40% used cooking oil methyl ester (40U).The test vehicles was drove following ECE + EUDC cycle. A series of testing test fuels was shown in Table 3.4 with 3 repeat. The average mass emissions and fuel consumption of used cooking oil methyl ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L were shown in Table 4.8 and 4.9.

Figure 4.1a shows plot between mass THC emissions of test vehicles and cooking oil methyl ester blended fuel, the Figure shown that THC mass emissions decreased with increased portions of used cooking oil methyl ester blended, However, mass THC emissions of Toyota D4D 2.5L has lower concentration than Isuzu DMAX 2.5L.

Figure 4.1b shows plot between CO emissions of test vehicles and cooking oil methyl ester blended fuels, the figure shown that CO mass emissions decreased with increased percent of used cooking oil methyl ester blended, However, mass CO emissions of Toyota D4D 2.5L has lower concentration than Isuzu DMAX 2.5L.

Figure 4.1c shows plot between NO_X emissions of test vehicles and cooking oil methyl ester blended fuel, the figure shows that NO_X mass emissions of Toyota D4D 2.5L increased with increased percent of used cooking oil methyl ester blended. But, Isuzu DMAX 2.5L shows did not difference, However, NO_X emissions of Toyota D4D 2.5L has lower concentration.

Figure 4.2d shows plot between CO_2 emissions of test vehicles and cooking oil methyl ester blended fuel, CO_2 mass emissions of test vehicles shows not significant difference with used cooking oil methyl ester blended. Toyota D4D 2.5L has higher CO_2 mass emissions, therefore, it was more complete combustion than Isuzu DMAX.

Figure 4.1e shows plot between PM emission of test vehicles and cooking oil methyl ester blended fuel, the plots show PM emissions of Toyota D4D 2.5L and Isuzu DMAX decreased with increasing of volume percent methyl ester blended fuels. Toyota D4D 2.5L shows higher PM emissions than Isuzu DMAX.

Figure 4.1f shows plot between fuel consumption of Toyota D4D 2.5L and Isuzu DMAX 2.5L and cooking oil methyl ester blended fuel, the plots show fuel consumption of two vehicles increased with increasing the portions of methyl ester blended. However, Isuzu DMAX has lower fuel consumption.

Table 4.8 The mass exhaust emissions and fuel consumption of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L.

Mass emissions	**BDS5**	**B20U**	**B30U**	**B40U**
THC (g/km)	0.037	0.024	0.035	0.035
CO (g/km)	0.435	0.421	0.463	0.489
NOx (g/km)	0.528	0.534	0.525	0.526
CO_2 (g/km)	224.324	225.987	224.448	226.091
PM (g/km)	0.090	0.070	0.061	0.57
Fuel consumption(l/100km)	8.274	8.659	8.658	8.781

Table 4.9 The mass exhaust emissions and fuel consumption of Used Cooking Oil Methyl Ester blended fuels on Isuzu DMAX 2.5L.

Mass emissions	**BDS5**	**B20U**	**B30U**	**B40U**
THC (g/km)	0.122	0.094	0.101	0.090
CO (g/km)	0.853	0.739	0.774	0.764
NOx (g/km)	0.754	0.787	0.805	0.803
CO_2 (g/km)	174.497	174.337	176.064	176.115
PM (g/km)	0.060	0.054	0.050	0.050
Fuel consumption(l/100km)	6.476	6.713	6.825	6.871

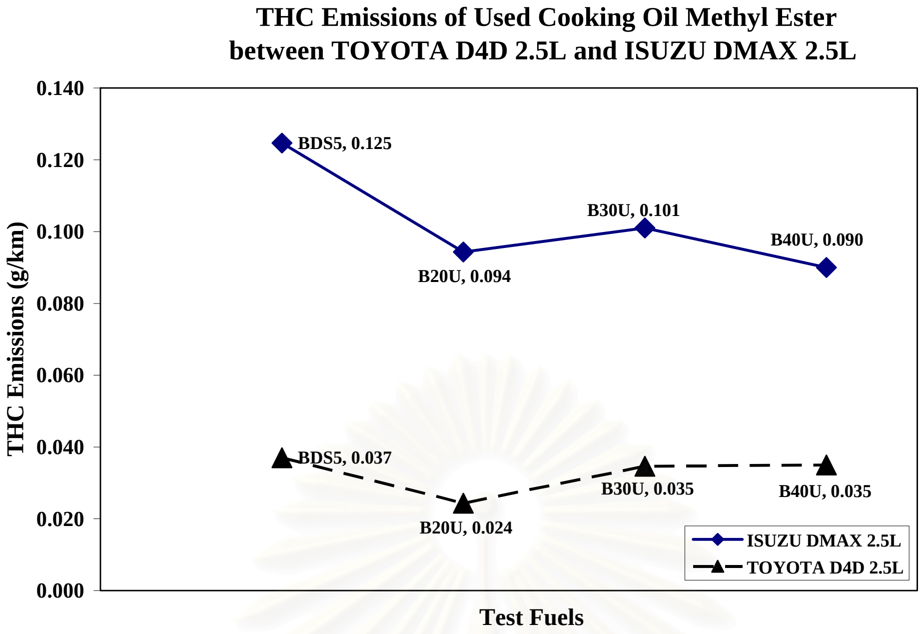


Figure 4.1a THC emissions of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

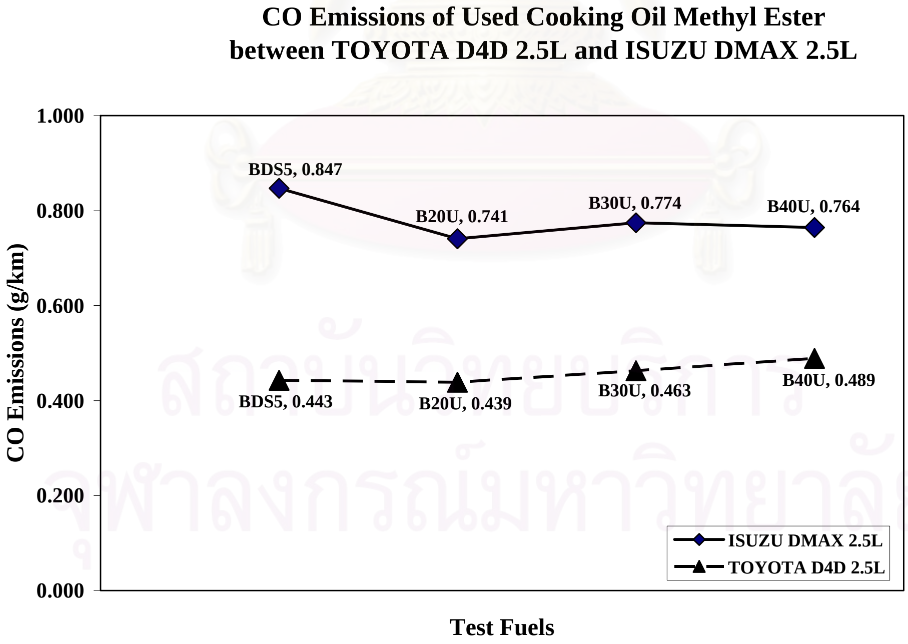


Figure 4.1b CO emissions of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

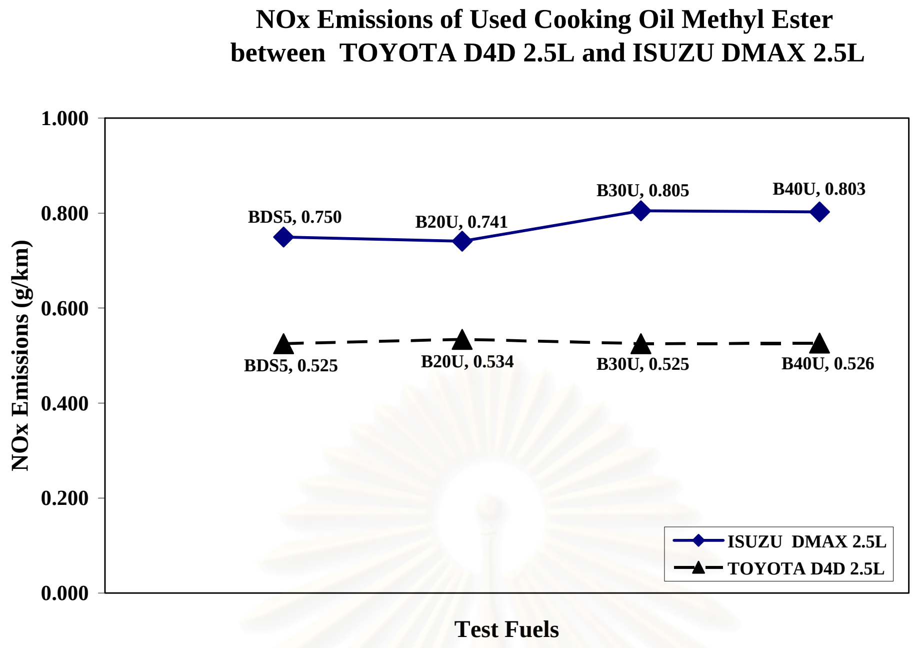


Figure 4.1c NOx emissions of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

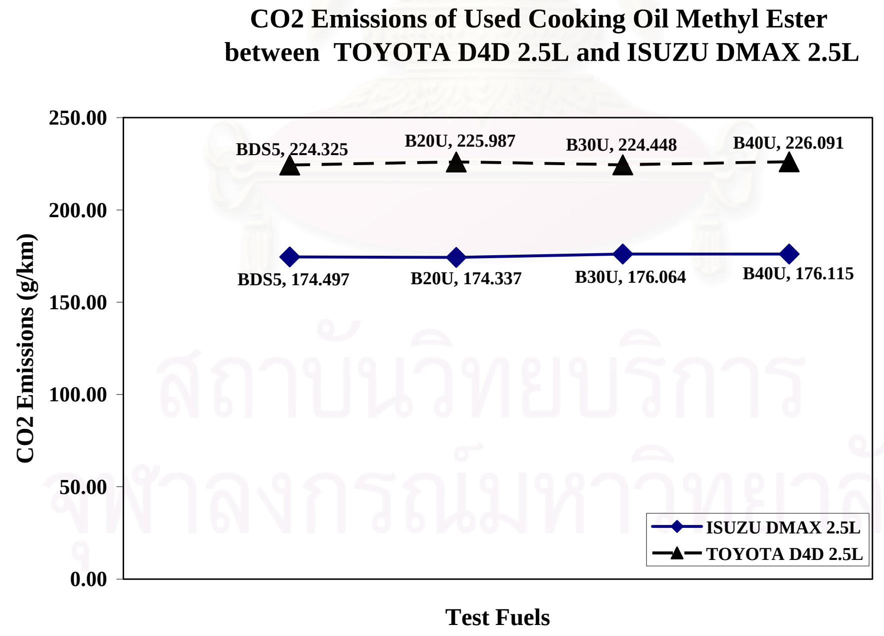


Figure 4.1d CO2 emissions of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

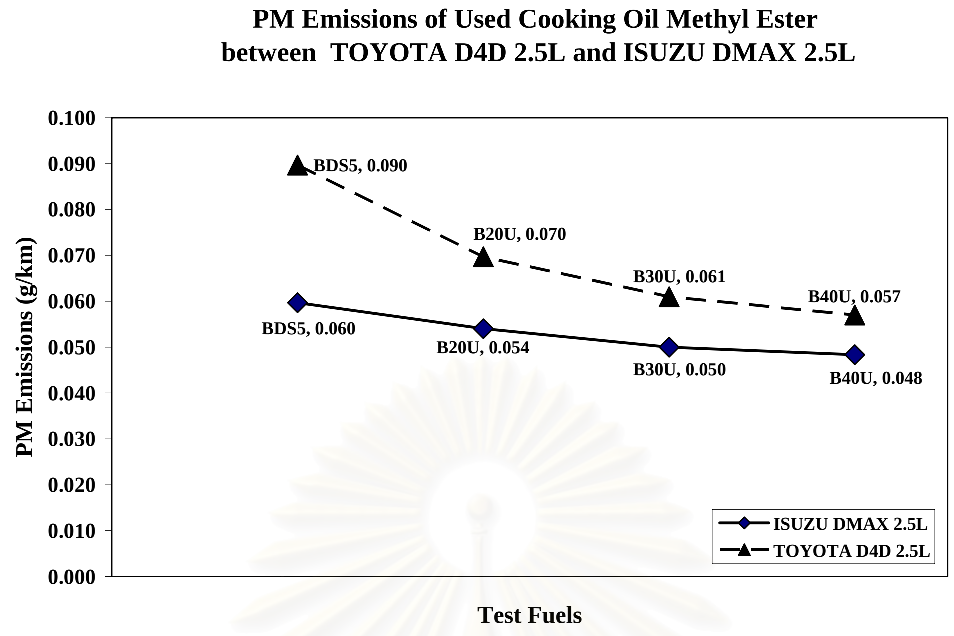


Figure 4.1e PM emissions of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

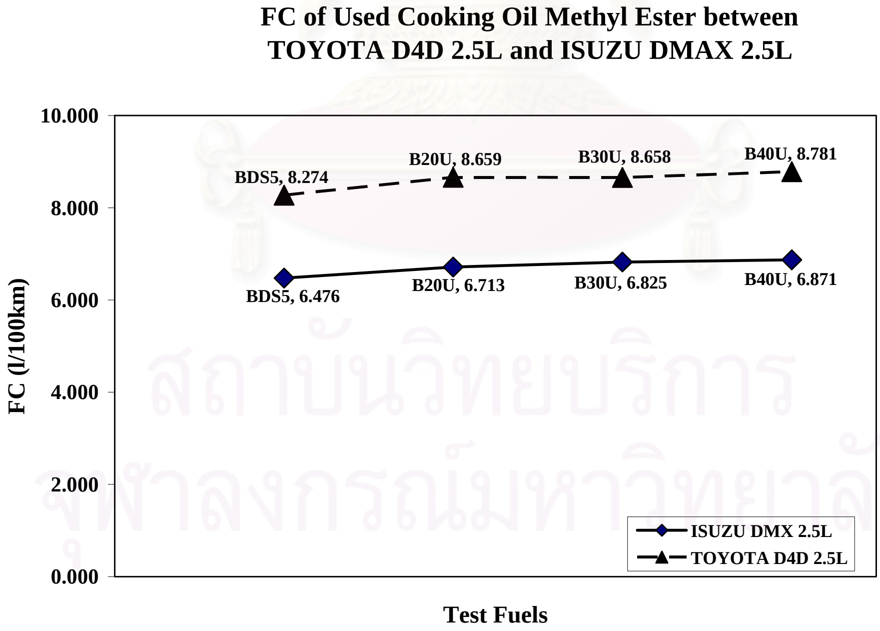


Figure 4.1f FC of Used Cooking Oil Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

Statistical analysis by T – test was used to comparing significant percent change of exhaust emissions and fuel consumption of B20U, B30U and B40U with BDS on Toyota D4D 2.5L and Isuzu DMAX 2.5L which shown in Table 4.10 and 4.11.

For Toyota D4D 2.5L fueled with 20U, the THC and PM in exhaust emissions were decreased to 34.01%, 22.15% respectively while fuel consumption increased to 4.66%. The PM in exhaust emissions was decreased to 31.88% while fuel consumption increased to 4.65% when Toyota D4D fueled with B30U. Toyota D4D 2.5L fueled with B40U showed in difference in exhaust emissions compared with base diesel except PM was decreased to 36.66% whereas fuel consumption was increased to 6.13%.

For Isuzu DMAX 2.5L fueled with B20U, the THC, CO, PM in exhaust emissions were decreased to 24.07%, 12.44% and 9.50% respectively, while fuel consumption were increased to 3.76%. B30U shows THC, CO, PM, which was decreased to 18.70%, 8.58% and 16.14% respectively while fuel consumption was increased to 5.39%. Isuzu DAMAX 2.5L fueled with B40U, the THC, CO and PM were decreased to 27.39%, 9.78% and 18.95% respectively, in the contrary the kinematics viscosity fuel consumption was increased to 6.10%.

Table 4.10 Statistical Analysis by T-test for the effect of Used Cooking Oil Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L.

% Change	**B20U**	**B30U**	**B40U**
THC	-34.01	-6.46(NS)	-5.48(NS)
CO	-1.20(NS)	+4.89(NS)	+10.32(NS)
NOx	+1.80(NS)	+0.03(NS)	+0.27(NS)
CO_2	+0.74(NS)	+0.06(NS)	+0.79
PM	-22.15	-31.88	-36.66
Fuel consumption	+4.66	+4.65	+6.13

Note: NS = Not significant difference.

Table 4.11 Statistical Analysis by T-test for the effect of Used Cooking Oil Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L.

% Change	**B20U**	**B30U**	**B40U**
THC	-24.07	-18.69	-27.39
CO	-12.44	-8.58	-9.78(NS)
NOx	+5.26(NS)	+7.37	+7.08
CO_2	-0.08(NS)	+0.09	+0.93(NS)
PM	-9.50	-16.14	-18.95
Fuel consumption	+3.76	+5.39	+6.10

Note: NS = Not significant difference.

4.4 The effect of Palm Stearin Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L and Isuzu DMAX 2.5L.

Toyota D4D 2.5L and Isuzu DMAX 2.5L were operated on chassis dynamometer which fueled with 5 kinds of test fuels: based diesel fuel, 2% palm stearin methyl ester (B2T), 5% palm stearin methyl ester (B5T), 20% palm stearin methyl ester (B20T) and 100% palm stearin methyl ester (B100T). The test vehicles were drove following ECE + EUDC cycle. Each test fuels were tested on a series that was shown in Table 3.4 with 3 repeat. The average mass emissions and fuel consumption of palm stearin methyl ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L were shown in Table 4.12 and 4.13.

Figure 4.2a shows the plot between THC mass emissions of test vehicles and palm stearin methyl ester blended fuels, the plots indicate that THC emissions decreased with increased volume of methyl ester blended. Toyota D4D 2.5L shows lower THC emissions than Isuzu DMAX 2.5L.

Figure 4.2b shows the plot between CO mass emissions of test vehicles and palm stearin methyl ester blended fuels, the figure shows that CO mass emission of B2T and B5T of two test vehicles show not difference in exhaust emissions, CO Emissions of B20T and B100T were decreased. Toyota D4D 2.5L has lower CO emissions than Isuzu DMAX 2.5L.

Figure 4.2c shows the plot between NO_X mass emissions of test vehicles and palm stearin methyl ester blended fuels, the plot indicate that NO_X emissions of two test vehicles were slightly increased with increasing volume percent of palm stearin methyl ester blended. However, Isuzu DMAX has higher NO_X emission than Toyota D4D 2.5L has.

Figure 4.2d shows the plot between CO_2 mass emissions of test vehicles and palm stearin methyl ester blended fuels, with increased volume of palm stearin methyl ester blended did not show a significantly increasing of CO_2. Toyota D4D 2.5L has higher CO_2 emissions than Isuzu DMAX 2.5L.

Figure 4.2e shows the plot between PM mass emissions of test vehicles and palm stearin methyl ester blended fuel. The figure shows that PM mass emissions decreased with increasing volume percent of palm stearin methyl ester blended. Especially B100T, PM emissions were decreased to 50-58% comparing with base diesel. Isuzu DMAX 2.5L has PM emissions higher than Toyota D4D.

Figure 4.2f shows the plot between fuel consumption of test vehicles and palm stearin methyl ester blended fuels. The plots show that B2T, B5T and B20T were not difference in fuel consumption comparing with base diesel fuel. However, for B100F increased to 8-10%. Isuzu DMAX 2.5L has lower fuel consumption.

4.12 The mass exhaust emissions and fuel consumption of Palm Stearin Methyl Ester blended on Isuzu DMAX 2.5L.

Mass emissions	**BDS1**	**B2T**	**B5T**	**BDS2**	**B20T**	**B100T**
THC (g/km)	0.052	0.046	0.046	0.052	0.038	0.035
CO (g/km)	0.556	0.558	0.570	0.547	0.451	0.440
NOx (g/km)	0.481	0.457	0.462	0.501	0.538	0.579
CO_2 (g/km)	223.467	221.262	223.376	221.337	219.398	227.535
PM (g/km)	0.075	0.073	0.080	0.065	0.059	0.027
Fuel consumption(l/100km)	8.555	8.527	8.617	8.475	8.527	9.257

4.13 The mass exhaust emissions and fuel consumption of Palm Stearin Methyl Ester blended on Isuzu DMAX 2.5L.

Mass emissions	**BDS1**	**B2T**	**B5T**	**BDS2**	**B20T**	**B100T**
THC (g/km)	0.134	0.121	0.128	0.122	0.102	0.054
CO (g/km)	0.845	0.827	0.870	0.831	0.765	0.518
NOx (g/km)	0.760	0.777	0.818	0.783	0.836	0.959
CO_2 (g/km)	210.339	208.528	207.948	210.365	212.625	214.310
PM (g/km)	0.099	0.100	0.090	0.092	0.086	0.046
Fuel consumption(l/100km)	8.083	8.063	8.057	8.085	8.287	8.70

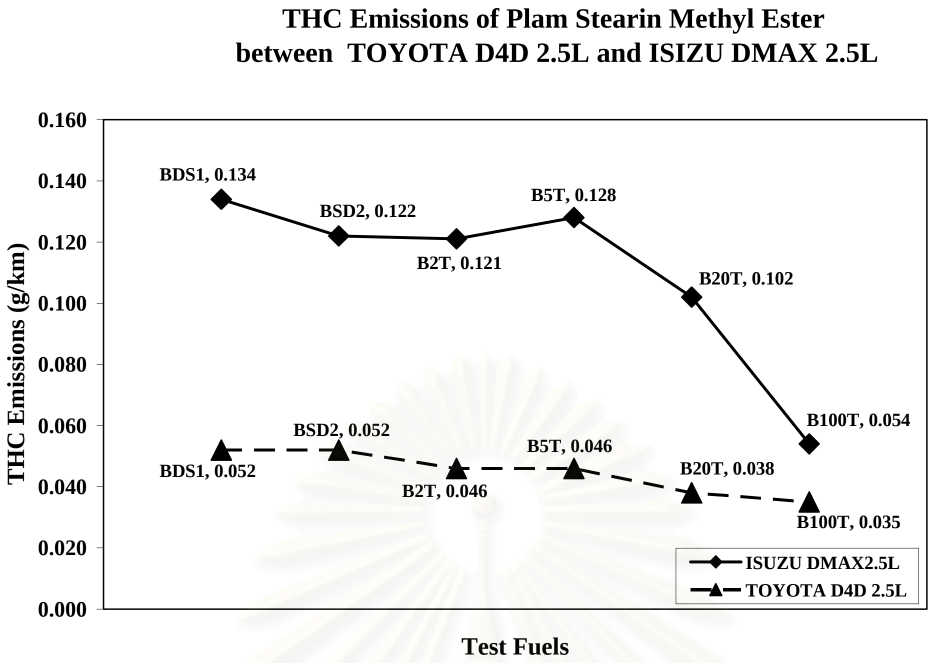


Figure 4.2a THC emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

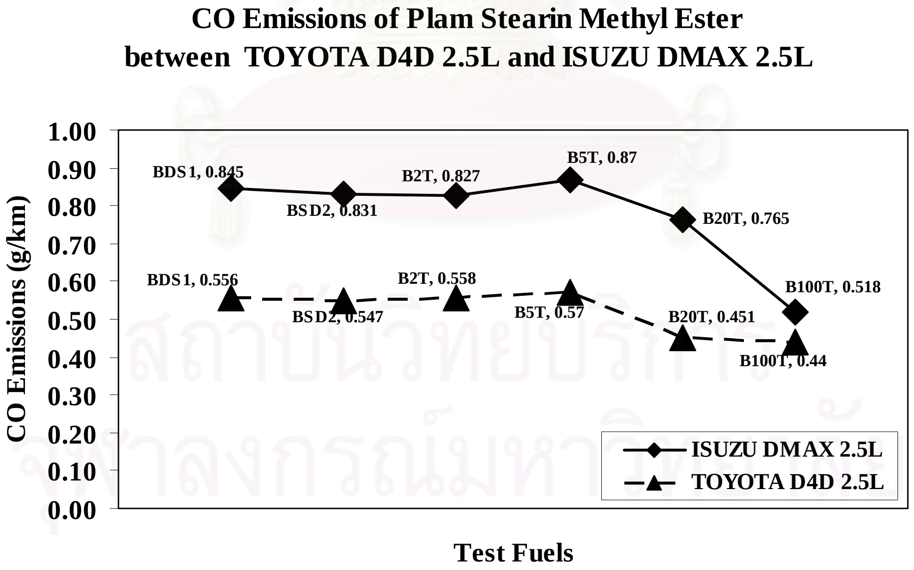


Figure 4.2b CO emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

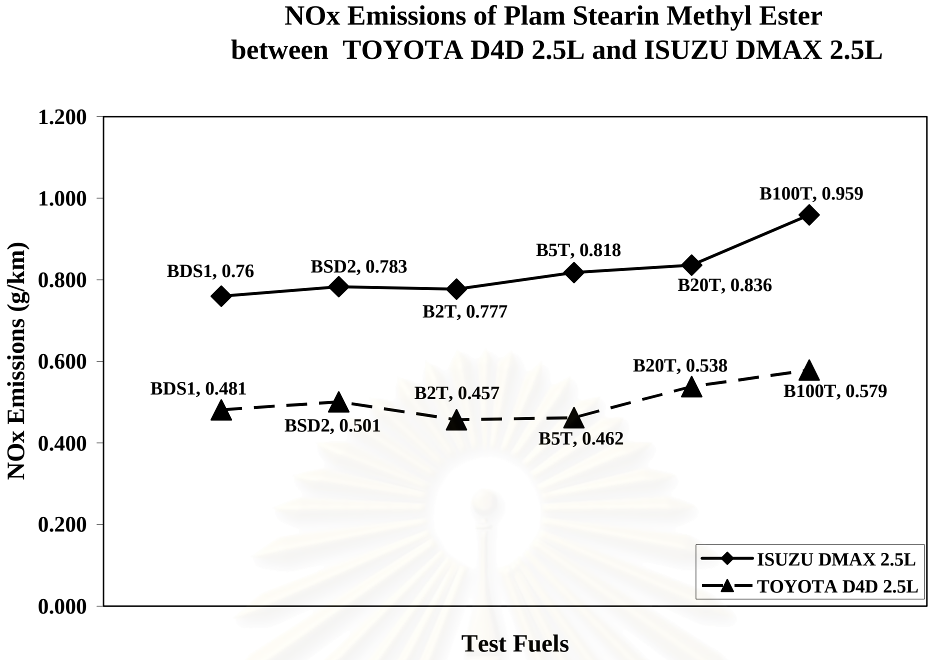


Figure 4.2c NOx emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

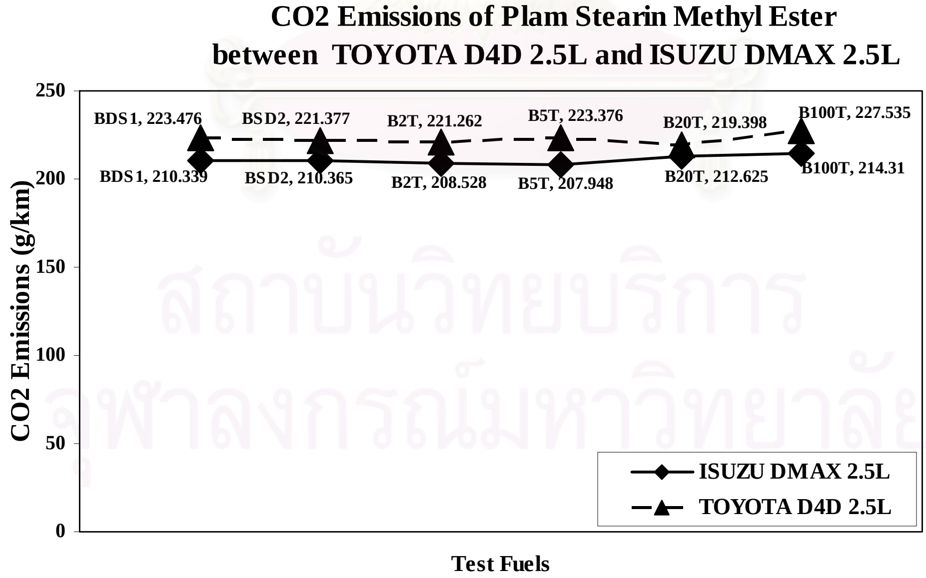


Figure 4.2d CO_2 emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

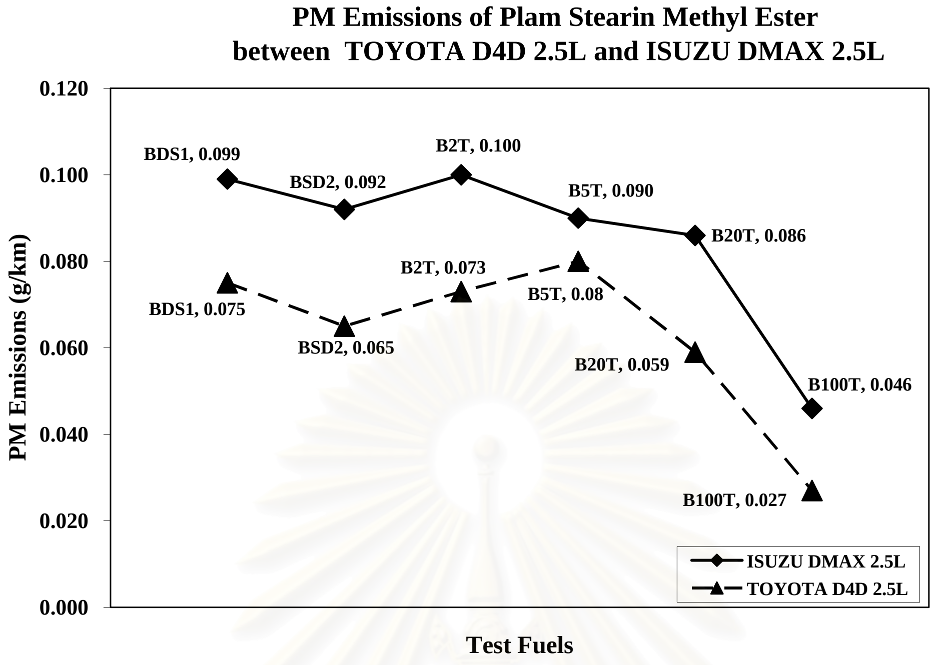


Figure 4.2e PM emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

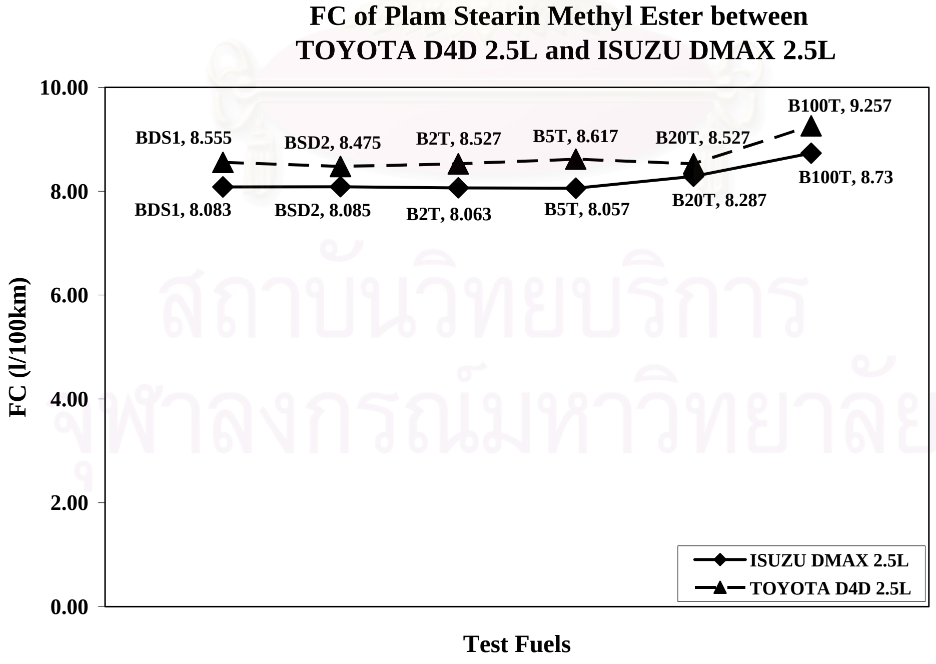


Figure 4.2f FC emissions of Palm Stearin Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

The statistical analysis by T – test using for comparing significant percent change of exhaust emissions and fuel consumption of B2T, B5T, B20T and B100T with BDS on Toyota D4D 2.5L and Isuzu DMAX 2.5L were shown in Table 4.14 and 4.15.

For Toyota D4D 2.5L fueled with B2T, the THC in exhaust emissions decreased about 12% that compared with base diesel, but fuel consumption did not difference. When fueled with B5T, the THC in exhaust emissions decreased to 11.50% while fuel consumption not difference. The THC, CO and PM in exhaust emissions when fueled B20T in Toyota D4D 2.5L decreased about 26.27%, 17.54 and 9.53 respectively, fuel consumption did not difference. Toyota D4D 2.5L fueled with pure palm stearin methyl ester (B100T), the THC, CO, PM in exhaust emissions decreased about 31.64%, 19.46%, 58.89% respectively. But, NOx emissions and fuel consumption increased 15.74% and 9% respectively.

For Isuzu DMAX 2.5L fueled with B2T, B5T not significant changes on exhaust emissions and fuel consumption compared with base diesel except the PM emissions of B5T decreased to 9.28%. When fueled with B20T, the THC, CO and PM decreased to 16.78%, 7.85%, 6.30% respectively. But, fuel consumption increased to 2.49% due to its calorific value lower than base diesel. Comparison exhaust emissions between B100T and base diesel show that the THC, CO and PM decreased to 55.54%, 37.60% and 50.36 respectively. But, NOx and fuel consumption increased 22.58% and 7.98%.

Table 4.14 Statistical Analysis by T-test for the effect of Palm Stearin Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L.

% Change	**B2T**	**B5T**	**B20T**	**B100T**
THC	-11.51	-11.50	-26.47	-31.64
CO	+0.27(NS)	+2.50(NS)	-17.54	-19.46
NOx	-4.98(NS)	-4.06	+7.46(NS)	+15.74
CO_2	-0.99	-0.04(NS)	-0.89	+2.78
PM	-2.68(NS)	-5.61(NS)	-9.53	-58.89
Fuel consumption	-0.33(NS)	+0.72(NS)	-0.61(NS)	+9.22

Note: NS = Not significant difference.

Table 4.15 Statistical Analysis by T-test for the effect of Palm Stearin Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L.

% Change	**B2T**	**B5T**	**B20T**	**B100T**
THC	-9.49(NS)	-4.56(NS)	-16.78	-55.54
CO	-2.13(NS)	+3.02(NS)	-7.85	-37.60
NO_X	+2.27(NS)	+7.67(NS)	+6.77	+22.58
CO_2	-0.86(NS)	-1.14(NS)	+1.07(NS)	+1.87
PM	+1.52(NS)	-9.28	-6.30	-50.36
Fuel consumption	-0.25(NS)	-0.33(NS)	+2.49	+7.98

Note: NS = Not significant difference.

4.5 The effect of Rapeseed Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L and Isuzu DMAX 2.5L.

Toyota D4D 2.5L and Isuzu DMAX 2.5L were operated on chassis dynamometer which fueled with 5 types of fuels: based diesel fuel, 2% rapeseed methyl ester (B2F), 5% rapeseed methyl ester (B5F), 20% rapeseed methyl ester (B20F) and 100% rapeseed methyl ester (B100F). The test vehicles were drove following to ECE + EUDC cycle. Each test vehicle was tested with test fuels in a series that shown in Table 3.4 with 3 repeat. The average mass emissions and fuel consumption of rapeseed methyl ester blended fuels of each test vehicles were shown in Table 4.16 and 4.17 respectively.

Figure 4.3a shows the plot between THC mass emissions of test vehicles and rapeseed methyl ester blended fuel. The plot shows that THC emissions of B2F, B5F were not significant difference in increasing. But, for THC emissions of B20F and B100F of Isuzu DMAX 2.5L and Toyota D4D 2.5L were decreased to 10 – 30 % comparing to base diesel fuel. Toyota D4D 2.5L shows lower THC emissions than Isuzu DMAX 2.5l.

Figure 4.3b shows the plot between CO mass emissions of test vehicles and rapeseed methyl ester blended fuel. THC emissions of B2F and B5F of test vehicles shows insignificant difference, However B20F and B100F increased CO emissions, Toyota D4D 2.5L has lower CO emissions than Isuzu DMAX has.

Figure 4.3c shows the plot between NO_X mass emissions of test vehicles and rapeseed methyl ester blended fuel. The figure shows NO_X emissions was increased with increasing volume percent of rapeseed methyl ester blended fuel. NO_X emissions from Toyota have higher than one from Isuzu DMAX 2.5L.

Figure 4.3d shows the plot between CO_2 mass emissions of test vehicles and rapeseed methyl ester blended fuel. Toyota D4D 2.5L has CO_2 emissions higher than Isuzu DMAX 2.5L, CO_2 emissions increased with increased volume of rapeseed methyl ester blended due to more oxygen contain in test fuels.

Figure 4.3e shows the plot between PM mass emissions of Toyota D4D 2.5L and Isuzu DMAX 2.5L with rapeseed methyl ester blended fuel. The plots show that the increase of volume percent of rapeseed methyl blended fuels leads to slightly decrease PM emissions and decrease largely with B100F while Isuzu DMAX 2.5L has also higher PM emissions.

Figure 4.3f shows the plot between fuel consumption of test vehicles and rapeseed methyl ester blended fuels. Toyota D4D 2.5L shows higher fuel consumption. The tendency of plot indicates that fuel consumption was increased with increasing volume percent of rapeseed methyl ester blended because methyl ester has lower gross heating value. In conclusion, Toyota 2.5L has higher fuel consumption than Isuzu DMAX 2.5L.

Table 4.16 The mass exhaust emissions and fuel consumption of Rapeseed Methyl Ester blended on Toyota D4D 2.5L.

Mass emissions	**BDS3**	**B2F**	**B5F**	**BDS4**	**B20F**	**B100F**
THC (g/km)	0.051	0.048	0.049	0.053	0.043	0.038
CO (g/km)	0.547	0.555	0.567	0.554	0.575	0.673
NOx (g/km)	0.526	0.520	0.534	0.527	0.546	0.588
CO_2 (g/km)	221.838	220.857	220.948	221.357	226.683	234.273
PM (g/km)	0.066	0.063	0.059	0.071	0.047	0.024
Fuel consumption(l/100km)	8.482	8.507	8.523	8.462	8.797	9.447

Table 4.17 The mass exhaust emissions and fuel consumption of Rapeseed Methyl Methyl Ester blended on Isuzu DMAX 2.5L.

Mass emissions	**BDS3**	**B2F**	**B5F**	**BDS4**	**B20F**	**B100F**
THC (g/km)	0.122	0.121	0.123	0.129	0.116	0.029
CO (g/km)	0.829	0.824	0.788	0.843	0.834	0.911
NOx (g/km)	0.780	0.830	0.806	0.758	0.844	1.017
CO_2 (g/km)	209.544	211.525	213.824	209.667	215.403	218.322
PM (g/km)	0.090	0.095	0.091	0.090	0.078	0.048
Fuel consumption(l/100km)	8.053	8.173	8.273	8.058	8.383	8.827

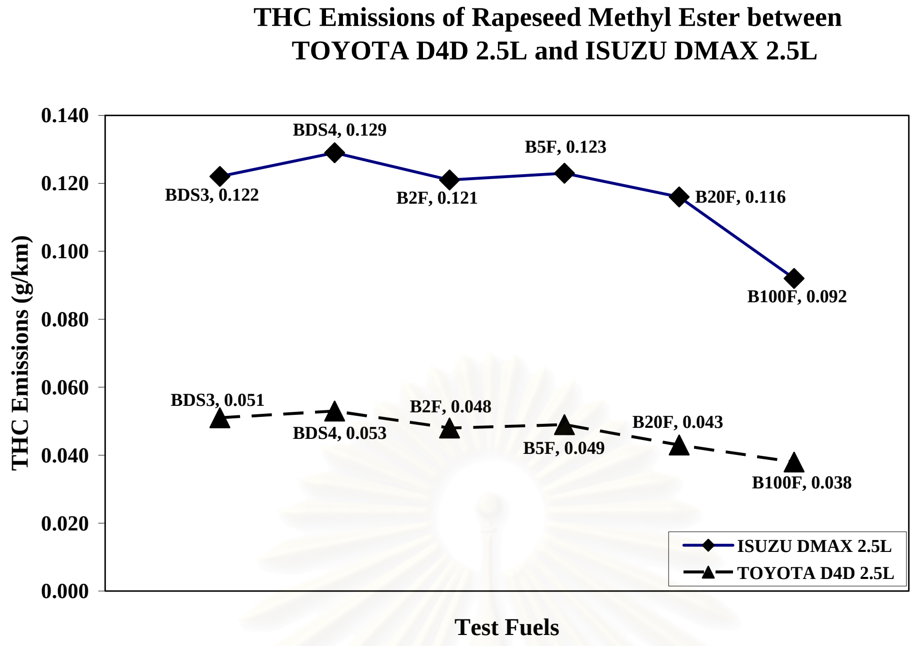

THC Emissions of Rapeseed Methyl Ester between TOYOTA D4D 2.5L and ISUZU DMAX 2.5L

Figure 4.3a THC emissions of Rapeseed Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

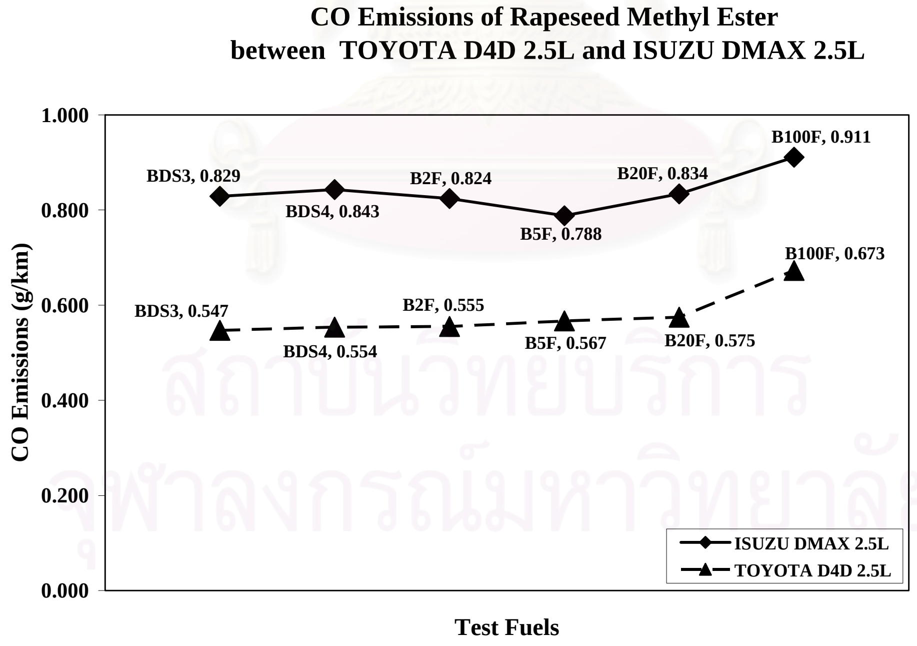

CO Emissions of Rapeseed Methyl Ester between TOYOTA D4D 2.5L and ISUZU DMAX 2.5L

Figure 4.3b CO emissions of Rapeseed Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

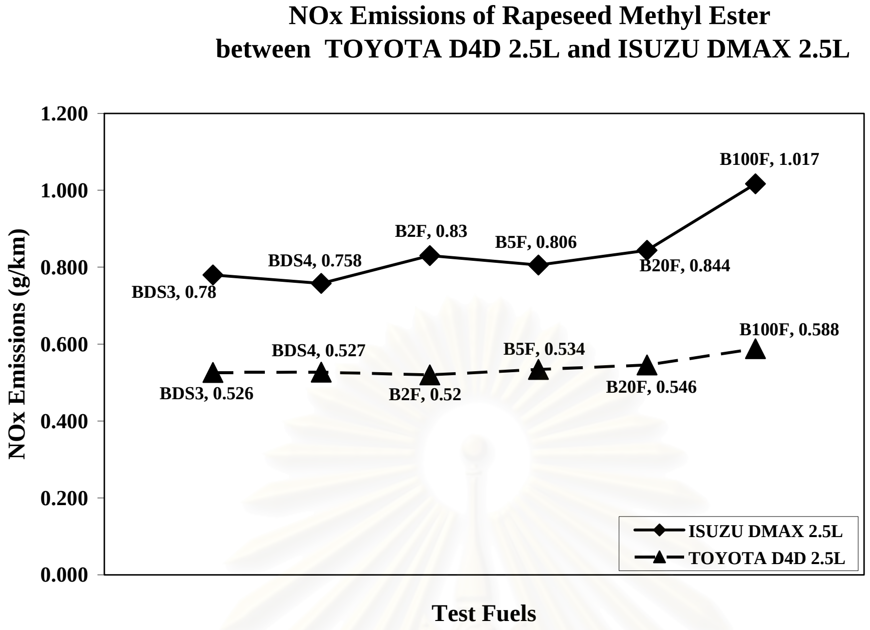


Figure 4.3c NOx emissions of Rapeseed Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

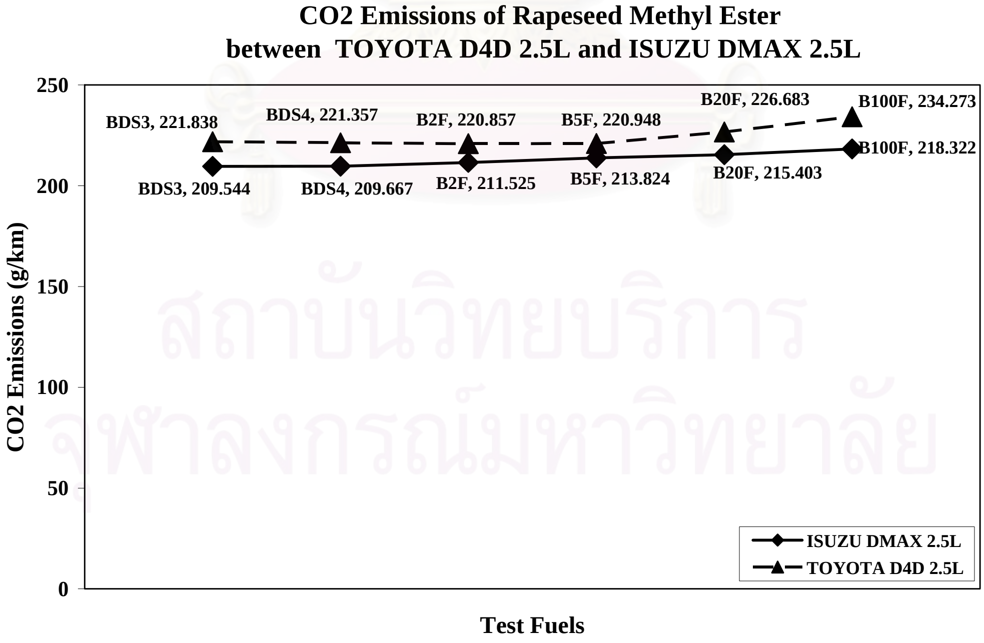


Figure 4.3d CO_2 emissions of Rapeseed Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

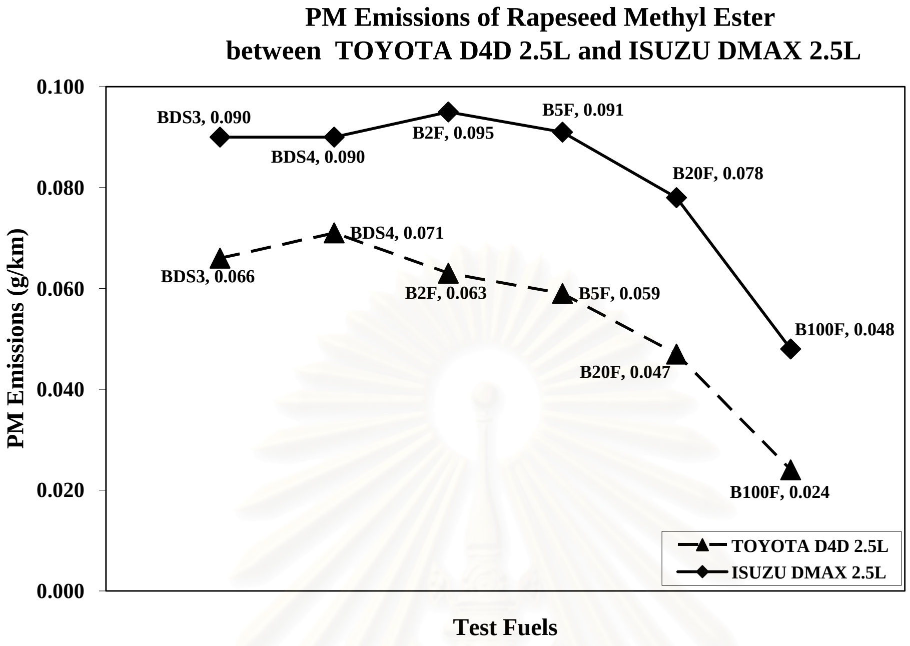


Figure 4.3e PM emissions of Rapeseed Methyl Ester blended fuels on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

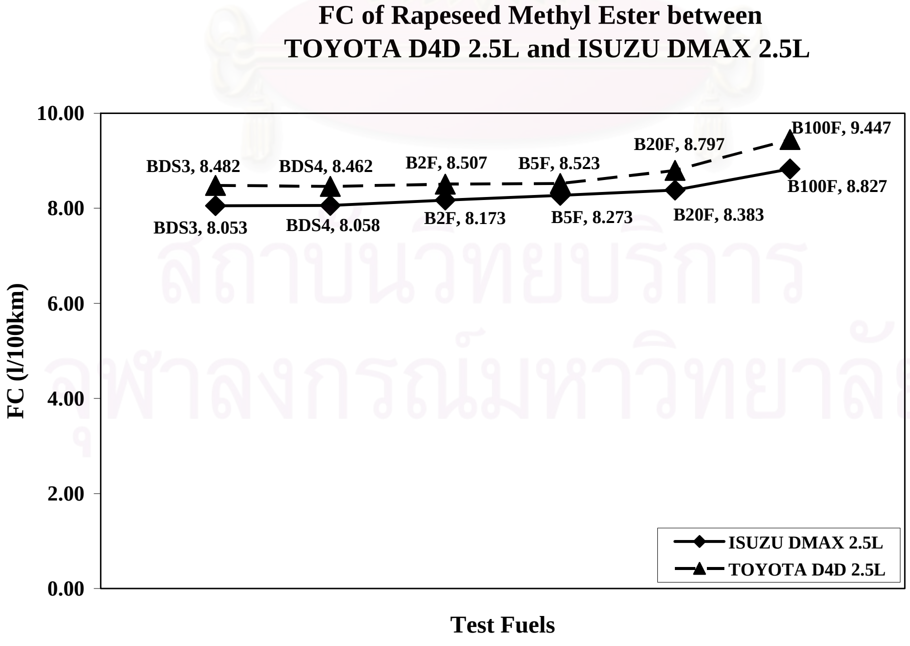


Figure 4.3f FC of Rapeseed Methyl Ester blended on Toyota D4D 2.5L and Isuzu DMAX 2.5L.

Statistical analysis by T-Test is used for comparison significant percent changed exhaust emissions and fuel consumption of rapeseed methyl ester, rapeseed methyl ester blended fuels with base diesel fuel. The results were shown in Table 4.18 and Table 4.19.

For Toyota D4D 2.5L fueled with B2Fand B5F, the THC, CO, NOx, emissions and fuel consumption did not show significant difference comparing with base diesel. But, B5F indicates that PM emission was decreased to 11%. THC and PM were decreased to about 17.47% and 33.90% respectively. Comparing to base diesel when fueled with B20F, CO emissions and fuel consumption were increased to 3.80% and 3.96 respectively. The exhaust emissions of B100F indicate that THC, PM were decreased to 26.98% and 66.67%, But NOx and CO and fuel consumption were increased to 11.75% and 21.64%, 11.64% respectively.

For Isuzu DMAX 2.5L, NOx in exhaust emissions and fuel consumption increased to 6.35%, 1.49% when fueled with B2F. B5F shows no effect on exhaust emissions, except fuel consumption, which was increased to 2.73%. The THC, PM of B20F were decreased to 10.91% and 14.01% respectively, However NOx and fuel consumption were increased 11.34% and 4.03%. B100F shows the THC, PM were decreased to 29.02% and 46.57%, But NOx and fuel consumption was increased to 35% and 9.53% respectively.

Table 4.18 Statistical Analysis by T-test for the effect of Rapeseed Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L.

% Change	**B2F**	**B5F**	**B20F**	**B100F**
THC	-5.55(NS)	-4.23(NS)	-17.47	-26.98
CO	+1.39(NS)	+3.56(NS)	+3.80	+21.64
NOx	-1.16(NS)	+1.58(NS)	+3.67(NS)	+11.75
CO_2	-0.44	-0.40(NS)	+2.41	+5.83
PM	-4.20(NS)	-10.58	-33.90	-66.67
Fuel consumption	+0.29(NS)	+0.49(NS)	+3.96	+11.64

Note: NS = Not significant difference.

Table 4.19 Statistical Analysis by T-test for the effect of Rapeseed Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L.

% Change	**B2F**	**B5F**	**B20F**	**B100F**
THC	-0.55(NS)	+0.80(NS)	-10.19	-29.02
CO	-0.43(NS)	-4.78(NS)	-1.07	+8.02
NOx	+6.35	+3.32(NS)	+11.34	+34.19
CO_2	+0.95	+2.04	+2.73	+4.13
PM	+5.50(NS)	+1.83(NS)	-14.01	-46.57
Fuel consumption	+1.49	+2.73	+4.03	+9.53

Note: NS = Not significant difference.

4.6 Comparison exhaust emissions and fuel consumption of palm stearin methyl ester and rapeseed methyl ester blended fuels for Toyota D4D and Isuzu DMAX.

Comparison exhaust emissions of palm stearin methyl ester blended fuels and rapeseed methyl ester blended fuels for Toyota D4D and Isuzu DMAX were shown in Table 4.20 and 4.21.

The results showed that palm strearin methyl ester blended fuels have lower the THC, CO, NO_X emissions than rapeseed methyl ester blended fuel with two test cars. Because of palm stearin methyl ester has smaller alkyl chain than rapeseed methyl ester which it would be easier to ignite in combustion chamber, but palm stearin methyl ester blended fuels have higher PM exhaust emissions than rapeseed methyl ester blended fuels were observed.

Table 4.20 Comparison exhaust emissions and fuel consumption of palm stearin methyl ester and rapeseed methyl ester blended fuels for Toyota D4D.

Test fuel/ emissions	THC (g/km)	CO (g/km)	NO_X (g/km)	CO_2 (g/km)	PM (g/km)	FC (l/100km)
BDS 1,2	0.052/ 0.052	0.556/ 0.547	0.481/ 0.501	223.467/ 221.337	0.075/ 0.065	8.555/ 8.475
BDS 3, 4	0.051/ 0.053	0.547/ 0.554	0.526/ 0.527	221.838/ 221.357	0.066/ 0.071	8.482/ 8.462
B2T	0.046	0.558	0.457	221.262	0.073	8.527
B2F	0.048	0.555	0.520	220.857	0.063	8.507
B5T	0.046	0.570	0.462	223.376	0.080	8.617
B5F	0.049	0.567	0.534	220.948	0.059	8,523
B20T	0.038	0.451	0.538	219.398	0.059	8.527
B20F	0.043	0.575	0.546	226.683	0.047	8.797
B100T	0.035	0.440	0.579	227.535	0.027	9.257
B100F	0.038	0.673	0.588	234.273	0.024	9.447

Table 4.21 Comparison exhaust emissions and fuel consumption of palm stearin methyl ester and rapeseed methyl ester blended fuels for Isuzu DMAX.

Test cars/ emissions	THC (g/km)	CO (g/km)	NO_X (g/km)	CO_2 (g/km)	PM (g/km)	FC (l/100km)
BDS 1,2	0.134/ 0.122	0.845/ 0.831	0.760/ 0.783	210.339/ 210.365	0.099/ 0.092	8.083/ 8.085
BDS 3, 4	0.122/ 0.129	0.829/ 0.843	0.780/ 0.758	209.544/ 209.667	0.090/ 0.090	8.053/ 8.058
B2T	0.121	0.827	0.777	208.528	0.100	8.063
B2F	0.121	0.824	0.830	211.525	0.095	8.173
B5T	0.128	0.870	0.818	207.948	0.090	8.057
B5F	0.123	0.788	0.806	213.824	0.091	8.273
B20T	0.102	0.765	0.836	212.625	0.086	8.287
B20F	0.116	0.834	0.844	215.403	0.078	8.383
B100T	0.054	0.518	0.959	214.310	0.046	8.700
B100F	0.029	0.911	1.017	218.322	0.048	8.827

CHAPTER V

CONCLUSIONS AND SUGGESTION

5.1 Conclusions

In this research, the effects of biodiesel blended fuels on exhaust emissions of diesel engines was investigated. Used cooking oil methyl ester was prepared from transesterification of used cooking oil with methanol in the presence of sodium hydroxide at temperature 60 °C for 1 hours. The used methyl ester was 70 – 80 %. Palm stearin methyl ester (PSME) was obtained from Thailand Institute of Science and Technological Research (TISTR). Rapeseed methyl ester (RME) was obtained from BIO-Diesel Wittenberge GmbH, Wittenbergeastm, Germany. These biodiesel were tested according to ASTM D 6751 specification. Palm stearin methyl ester, rapeseed methyl ester were blended with base diesel in ratio 2, 5, 20 volume percent and used cooking oil methyl in ratio 20, 30, 40 volume percent, all biodiesel blended fuels were tested according to Department of Energy Business standard. Two test vehicles were Toyota D4D 2.5L and Isuzu DMAX 2.5L which operated all biodiesel blended fuels on chassis dynamometer and droved following Euro 3 drive cycle with 3 repeat. Exhaust emissions and fuel consumption of biodiesel blended fuels were obtained and compared with based diesel. The conclusions of this study are following:

1. Biodiesel blended with diesel fuel did not affect the chemical and physical properties of diesel fuel, except slightly increasing in viscosity and lower heating value than diesel fuel were observed. Moreover, 2% and 5% biodiesel blended fuels were improved lubricity performance of diesel fuel.

2. Particulate emissions reduced as the concentration of any of the tested biodiesel fuels were increased in the blend. These reductions are mainly justified by increase in oxygen content in the fuel which contributes to a complete fuel oxidation even in locally rich zone, and by lower final boiling point.

3. The presence of biodiesel in the fuel leads to an increased NO_X emissions, the oxygen in biodiesel may did not cause of the observed NO_X increased, but this does not explain the lack of NO_X increase in this study. It is possible that other properties of biodiesel or interaction with characteristics of the fuel injection process and combustion chamber dynamics may cause variation in the expected trend toward higher NO_X.

4. Biodiesel blended with base diesel leads to a consider decrease of CO and HC emissions. These reduction partly be due to the oxygen in the blended allows more CO and HC to be oxidized to CO_2.

5. Compared fuel consumption of biodiesel and its blends with diesel fuel. Fuel consumption were slightly increased as the biodiesel concentration is increased in the blended. The net calorific value of biodiesel is about 12% lower than that of diesel fuel. This may explain the increasing fuel consumption.

6. Palm strearin methyl ester blended fuels have lower the THC, CO, NO_X emissions than rapeseed methyl ester blended fuel with two test cars. Because of palm stearin methyl ester has smaller alkyl chain than rapeseed methyl ester which it would be easier to ignite in combustion chamber, but palm stearin methyl ester blended fuels have higher PM exhaust emissions than rapeseed methyl ester blended fuels were observed.

7. The blends of 2% palm stearin methyl ester and rapeseed methyl ester showed not be significant difference in exhaust emissions and fuel consumption comparing to based diesel.

8. The blends of 5% palm stearin methyl ester and rapeseed methyl ester showed tendency the reduction of THC and PM emissions while fuel consumption did not different.

9. The blends of 20% palm stearin methyl ester, rapeseed methyl ester and used cooking oil methyl ester, the THC, PM emissions were decreased to 10 – 34% and 6 – 34% respectively while the fuel consumption was increased 2 – 5%.

10. The blends of 30, 40% used cooking oil methyl ester, the THC, PM emissions were decreased 18 – 27% and 11 – 36%, but NO_X emissions and fuel consumption were increased to 7%, 5 – 6% respectively.

11. Pure palm stearin methyl ester and rapeseed methyl ester shows decreasing of all exhaust emissions, but NO_X emissions and fuel consumption were increased.

5.2 Suggestion for future work

1. The blends of 2% methyl ester improved lubricity performance, So, using methyl ester as lubricity additive should be study and research**.**
2. The utilization of methyl ester in the future needs more studies in engine performance tests, durability test**.**

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APPENDICES

APPENDIX A

Fuel consumption calculation by carbon balance method

Calculation of fuel consumption by carbon balance method

FC = (Density of test fuels g/l) / (Mw HC + (CO_2/44) + (CO/28) + (HC/Mw HC)

Mw HC = (12 + (H_f / C_f) + (16*O_f / C_f)

H_f = Percent of hydrogen in fuels
C_f = Percent of carbon in fuels
O_f = Percent of oxygen in fuels

CO_2 = CO_2 contain in exhaust emissions (g/km)
CO= CO contain in exhaust emissions (g/km)
HC = HC contain in exhaust emissions (g/km)

For example: Calculation of FC in base diesel

FC = (Density of test fuel) / (Mw HC + (CO_2/44) + (CO/28) + (HC/Mw HC)

Density of fuels = 857.0 g/l
H_f = 84
C_f = 13
O_f = 0
Mw HC = (12 + (H_f / C_f) + (16*O_f / C_f)
Mw HC = (12 + (84 / 13) + (16*0 / 13)
Mw HC = 13.857
CO_2 = 222.345 (g/km)
CO= 0.407 (g/km)
HC = 0.038 (g/km)

FC = (857.0) / (13.857 + (222.345/44) + (0.407/28) + (0.038/13.857)
FC = 12.20 km/l

The calculation for fuel consumption of other test fuels as follow B2T, B5T, B20T, B100T, B2F, B5F, B20F, B100F, B20U, B30U, B40U were the same as the base diesel fuel calculation.

APPENDIX B

Calculation the significant percent change of exhaust emissions by using T-test

Calculation the significant percent change of exhaust emissions by using T-test

The t-test is the most commonly used method to evaluate the differences in means between two groups. The t-test can be used even if the samples size are very small.

Example 1 for calculation the significant percent change of exhaust emissions by using T-test

Comparison THC emissions of Toyota D4D 2.5L between base diesel and B20U

No.	Diesel	B20U	% Change
1	0.038	0.020	-47.368
2	0.036	0.028	-22.222
3	0.037	0.025	-32.432
Average % change			-34.007

Standard deviation (SD) = 12.646

Number of Data (N) = 3

Probability (b) = 0.05

Degree of freedom (d) = 2

T-value of the Student's t-distribution for the term above = 4.303 (t- table)

Standard error = (T-value) * SD / $\sqrt{N}$

= 31.416

x-error = Average % change – Standard error

= -34.007-31.416

= -65.424

x+error= Average % change + Standard error

= -34.007 + 31.416

= -2.591

The range of HC emission reduction compared with base diesel was between -2.591 to -65.424%, average value -34.242. Therefore, B20U showed significant reduction of THC emission.

Example 2 for calculation the significant percent change of exhaust emissions by using T-test

Comparison CO emissions of Toyota D4D 2.5L between base diesel and B20U

No.	Diesel	B20U	% Change
1	0.407	0.380	-6.634
2	0.462	0.461	-0.216
3	0.460	0.475	+3.260
		Average % change	-1.196

Standard deviation (SD) = 5.019
Number of Data (N) = 3
Probability (b) = 0.05
Degree of freedom (d) = 2
T-value of the Student's t-distribution for the term above = 4.303 (t- table)

Standard error = (T-value) * SD / √N
= 4.303 * 5.019 / √3
= 12.469
x-error = Average % change – Standard error
= -1.196-12.469
= -13.666
x+error= Average % change + Standard error
= -1.196+12.469
= 11.273

The range of CO emission reduction compared with base diesel was between -13.666 to +11.273%, average value -1.196%. Therefore, B20U showed not significant reduction of CO emission.

The calculation for significant percent change of exhaust emissions and fuel consumption by using T-test of other test fuels with base diesel fuel as follow B2T, B5T, B20T, B100T, B2F, B5F, B20F, B100F, B20U, B30U, B40U were the same as Example 1 and 2 calculation.

Statistical Analysis by T-test for the effect of Palm Stearin Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L

% Change	**B2T**	**B5T**	**B20T**	**B100T**
THC	-11.51	-11.50	-26.47	-31.64
CO	+0.27(NS)	+2.50(NS)	-17.54	-19.46
NOx	-4.98(NS)	-4.06	+7.46(NS)	+15.74
CO$_2$	-0.99	-0.04(NS)	-0.89	+2.78
PM	-2.68(NS)	-5.61(NS)	-9.53	-58.89
Fuel consumption	-0.33(NS)	+0.72(NS)	-0.61(NS)	+9.22

Note: NS = Not significant difference

Statistical Analysis by T-test for the effect of Palm Stearin Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L

% Change	**B2T**	**B5T**	**B20T**	**B100T**
THC	-9.49(NS)	-4.56(NS)	-16.78	-55.54
CO	-2.13(NS)	+3.02(NS)	-7.85	-37.60
NO$_X$	+2.27(NS)	+7.67(NS)	+6.77	+22.58
CO$_2$	-0.86(NS)	-1.14(NS)	+1.07(NS)	+1.87
PM	+1.52(NS)	-9.28	-6.30	-50.36
Fuel consumption	-0.25(NS)	-0.33(NS)	+2.49	+7.98

Note: NS = Not significant difference

Statistical Analysis by T-test for the effect of Rapeseed Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L

% Change	**B2F**	**B5F**	**B20F**	**B100F**
THC	-5.55(NS)	-4.23(NS)	-17.47	-26.98
CO	+1.39(NS)	+3.56(NS)	+3.80	+21.64
NOx	-1.16(NS)	+1.58(NS)	+3.67(NS)	+11.75
CO_2	-0.44	-0.40(NS)	+2.41	+5.83
PM	-4.20(NS)	-10.58	-33.90	-66.67
Fuel consumption	+0.29(NS)	+0.49(NS)	+3.96	+11.64

Note: NS = Not significant difference

Statistical Analysis by T-test for the effect of Rapeseed Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L

% Change	**B2F**	**B5F**	**B20F**	**B100F**
THC	-0.55(NS)	+0.80(NS)	-10.19	-29.02
CO	-0.43(NS)	-4.78(NS)	-1.07	+8.02
NOx	+6.35	+3.32(NS)	+11.34	+34.19
CO_2	+0.95	+2.04	+2.73	+4.13
PM	+5.50(NS)	+1.83(NS)	-14.01	-46.57
Fuel consumption	+1.49	+2.73	+4.03	+9.53

Note: NS = Not significant difference

Statistical Analysis by T-test for the effect of Used Cooking Oil Methyl Ester blended fuels on exhaust emissions and fuel consumption of Toyota D4D 2.5L

% Change	**B20U**	**B30U**	**B40U**
THC	-34.01	-6.46(NS)	-5.48(NS)
CO	-1.20(NS)	+4.89(NS)	+10.32(NS)
NOx	+1.80(NS)	+0.03(NS)	+0.27(NS)
CO_2	+0.74(NS)	+0.06(NS)	+0.79
PM	-22.15	-31.88	-36.66
Fuel consumption	+4.66	+4.65	+6.13

Note: NS = Not significant difference

Statistical Analysis by T-test for the effect of Used Cooking Oil Methyl Ester blended fuels on exhaust emissions and fuel consumption of ISUZU DMAX 2.5L

% Change	**B20U**	**B30U**	**B40U**
THC	-24.07	-18.69	-27.39
CO	-12.44	-8.58	-9.78(NS)
NOx	+5.26(NS)	+7.37	+7.08
CO_2	-0.08(NS)	+0.09	+0.93(NS)
PM	-9.50	-16.14	-18.95
Fuel consumption	+3.76	+5.39	+6.10

Note: NS = Not significant difference

APENDIX C
Biodiesel specification according to ASTM D 6751

Biodiesel specification according to ASTM D 6751

Property	**Test Method**	**Grade S15 Limits**	**Grade S500 Limits**	**Units**
Flash point (closed cup)	D 93	130.0 min	130.0 min	°C
Water and sediment	D2709	0.050 max	0.050 max	% volume
Kinematic viscosity, 40 °C	D445	1.9-6.0^{C}	1.9-6.0^{C}	mm^2/s
Sulfate ash	D874	0.020max	0.020max	% mass
Sulfur^{D}	D5453	0.0015max(15)	0.05max(500)	%mass(ppm)
Copper strip corrosion	D130	No. 3 max	No. 3 max	
Cetane number	D613	47 min	47 min	
Cloud point	D2500	Report^{E}	Report^{E}	°C
Carbon residue^{F}	D4530	0.050max	0.050max	% mass
Acid number	D664	0.80max	0.80max	mg KOH/g
Free glycerine	D 6584	0.020	0.020	% mass
Total glycerine	D 6584	0.240	0.240	% mass
Phosphorus content	D4951	0.001max	0.001max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90% recovered	D1160	360max	360max	°C

[A] To meet special operating conditions of individual limit requirements may me agreed upon between purchaser, seller, and manufacturer.

[B] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 5.1.

[C] See X1.3.1. The 6.0 mm^2/s upper viscosity limit is higher than petroleum based diesel fuel and should be taken into consideration when blending.

[D] Other sulfur limits can apply in selected areas in the United Stated and in other countries.

[E] The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending

[F] Carbon residue shall be run on the 100% sample

APPENDIX D

Diesel specification according to Department of Energy Business standard. (vol. 2) 2004

Diesel specification according to Department of Energy Business Standard (vol. 2) 2004

No.	Specifications	Rate	Diesel Fuel		Test Method
			HSD	LSD	
1	Specific Gravity at 15.6/15.6 ^{o}C	min	0.81	-	ASTM D 1298
		max	0.87	0.920	
2	Cetane Number or	min	47	45	ASTM D 613
	Calculated Cetane Index				ASTM D 976
3	Viscosity, *cSt.*				ASTM D 445
	3.1 at 40 ^{o}C	min	1.8	-	
		max	4.1	8.0	
	3.2 at 50 ^{o}C	min	-	-	
		max	-	6.0	
4	Pour Point, ^{o}C	max	10	16	ASTM D 97
5	Sulphur Content, *%wt.*	max	0.035	1.5	ASTM D 2622
6	Copper Strip Corrosion	max	No. 1	-	ASTM D 130
7	Carbon Residue, *%wt.*	max	0.05	-	ASTM D 189
8	Water and Sediment, *%vol.*	max	0.05	0.3	ASTM D 2709
9	Ash, *%wt.*	max	0.01	0.02	ASTM D 482
10	Flash Point, ^{o}C	min	52	52	ASTM D 93
11	Distillation, ^{o}C				
	90% Recovered	max	357	-	ASTM D 86
12	Colour	min	-	4.5	ASTM D 1500
		max	4.0	7.5	
13	Lubricity by HFRR, μm	max	460	-	CEC F- 06-A-96
14	Additives				

VITA

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